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An Introduction to *Ab Initio* Molecular Dynamics Simulations

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An introduction into the basic ideas of *ab initio* molecular dynamics methods is given. These methods unify molecular dynamics simulations and electronic structure calculations in the sense that the interactions, i.e. the forces used to propagate the classical nuclei, are obtained from concurrent or "on the fly" electronic structure calculations. Several such molecular dynamics schemes are discussed which arise from a sequence of approximations to the fully coupled Schrödinger equation for electrons and nuclei. Special attention is devoted to Car–Parrinello methods being characterized by a fictitious dynamics of the electronic degrees of freedom.

1 Introduction

Classical molecular dynamics using "predefined potentials", either based on empirical data or on independent electronic structure calculations, is well established as a powerful tool to investigate many–body condensed matter systems. The broadness, diversity, and level of sophistication of this technique is documented in several monographs as well as proceedings of conferences and scientific schools[4, 47, 118, 88, 26, 22, 72, 267, 220]. At the very heart of any molecular dynamics scheme is the question of how to describe – that is in practice how to approximate – the interatomic interactions. The traditional route followed in molecular dynamics is to determine these potentials in advance. Typically, the full interaction is broken up into two–body, three–body and many–body contributions, long–range and short–range terms etc., which have to be represented by suitable functional forms, see Section 2 of Ref. 108 for a detailed account. After decades of intense research, very elaborate interaction models including the non–trivial aspect to represent them analytically were devised[108, 226, 243].

Despite overwhelming success – which will however not be praised in these Lecture Notes – the need to devise a "fixed model potential" implies serious drawbacks, see the introduction sections of several earlier reviews[222, 201] for a more complete digression on these aspects. Among the most delicate ones are systems where (i) many different atom or molecule types give rise to a myriad of different interatomic interactions that have to be parameterized and / or (ii) the electronic structure and thus the bonding pattern changes qualitatively in the course of the simulation. These systems can be called "chemically complex".

The reign of traditional molecular dynamics *and* electronic structure methods was greatly extended by the family of techniques that is called here "*ab initio* molecular dynamics", see Ref. 179 for a comprehensive account. Other names that are currently in use are for instance first principles, on–the–fly, direct, extended Lagrangian, quantum chemical, Hellmann–Feynman, potential–free, or just quantum molecular dynamics among others.

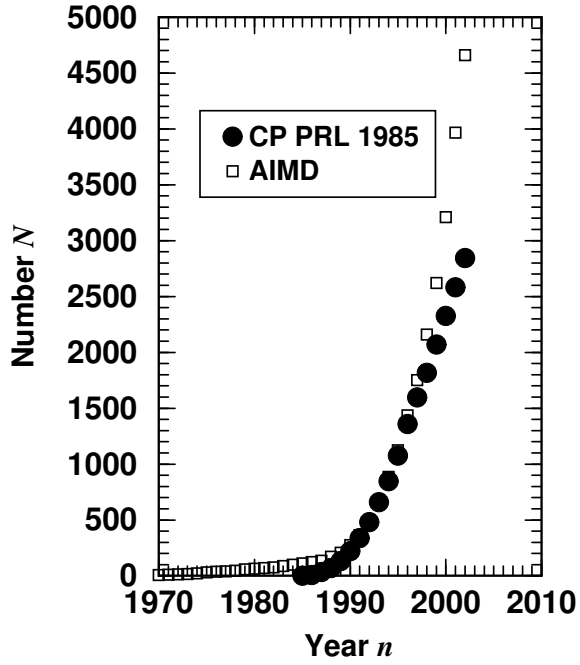

Figure 1. Publication and citation analysis up to the year 2002. Squares: number of publications N which appeared up to the year n containing the keyword "ab initio molecular dynamics" (or synonyms such as "first principles MD", "Car–Parrinello simulations" etc.) in title, abstract or keyword list. Circles: number of publications N which appeared up to the year n citing the 1985 paper by Car and Parrinello[38] (including misspellings of the bibliographic reference). Self–citations and self–papers are excluded, i.e. citations of Ref. 38 in their own papers and papers co-authored by R. Car and / or M. Parrinello are *not* considered in the respective statistics. The analysis is based on the CAPLUS ("Chemical Abstracts Plus"), INSPEC ("Physics Abstracts"), and SCI ("Science Citation Index") data bases at STN International. Updated statistics as of 05.05.2003 based on data reported in Refs. 178, 179, 181.

The basic idea underlying every *ab initio* molecular dynamics method is to compute the forces acting on the nuclei from electronic structure calculations that are performed "on–the–fly" as the molecular dynamics trajectory is generated. In this way, the electronic variables are not integrated out beforehand, but are considered as active degrees of freedom. This implies that, given a suitable approximate solution of the many–electron problem, also "chemically complex" systems can be handled by molecular dynamics. But this also implies that the approximation is shifted from the level of selecting the model potential to the level of selecting a particular approximation for solving the Schrödinger equation.

Applications of *ab initio* molecular dynamics are particularly widespread in materials science and chemistry, where the aforementioned difficulties (i) and (ii) are particularly severe. The power of this novel technique lead to an explosion of the activity in this field in terms of the number of published papers. The locus can be located in the late–eighties, see the squares in Figure 1 that can be interpreted as a measure of the activity in the area of *ab initio* molecular dynamics. As a matter of fact the time evolution of the number of citations of a particular paper, the one by Car and Parrinello from 1985 entitled "Unified Approach

for Molecular Dynamics and Density–Functional Theory"[38], parallels the trend in the entire field, see the circles in Figure 1. Thus, the resonance that the Car and Parrinello paper evoked and the popularity of the entire field go hand in hand in the last decade. Incidentally, the 1985 paper by Car and Parrinello is the last one included in the section "Trends and Prospects" in the reprint collection of "key papers" from the field of atomistic computer simulations[47]. That the entire field of *ab initio* molecular dynamics has grown mature is also evidenced by a separate PACS classification number (71.15.Pd "Electronic Structure: Molecular dynamics calculations (Car–Parrinello) and other numerical simulations") that was introduced in 1996 into the *Physics and Astronomy Classification Scheme*[211].

Despite its obvious advantages, it is evident that a price has to be payed for putting molecular dynamics on *ab initio* grounds: the correlation lengths and relaxation times that are accessible are much smaller than what is affordable in the framework of standard molecular dynamics. More recently, this caveat got counterbalanced by the ever increasing power of available computing resources, in particular massively parallel platforms[141], which shifted many problems in the physical sciences right into the realm of *ab initio* molecular dynamics. Another appealing feature of standard molecular dynamics is less evident, namely the "experimental aspect of playing with the potential". Thus, tracing back the properties of a given system to a simple physical picture or mechanism is much harder in *ab initio* molecular dynamics. On the other hand it has the power to eventually put phenomena onto a firm basis in terms of the underlying electronic structure and chemical bonding pattern. Most importantly, however, is the fact that new phenomena, which were not foreseen before starting the simulation, can simply happen if necessary. This gives *ab initio* molecular dynamics a truly predictive power.

Ab nitio molecular dynamics can also be viewed from another corner, namely from the field of classical trajectory calculations[270, 228]. In this approach, which has its origin in gas phase molecular dynamics, a *global* potential energy surface is constructed in a first step either empirically or based on electronic structure calculations. In a second step, the dynamical evolution of the nuclei is generated by using classical mechanics, quantum mechanics or semi / quasiclassical approximations of various sorts. In the case of using classical mechanics to describe the dynamics – the focus of the present overview – the limiting step for large systems is the first one, why so? There are $3N-6$ internal degrees of freedom that span the global potential energy surface of an unconstrained N–body system. Using for simplicity 10 discretization points per coordinate implies that of the order of 10^{3N-6} electronic structure calculations are needed in order to map such a global potential energy surface. Thus, the computational workload for the first step grows roughly like $\sim 10^N$ with increasing system size. This is what might be called the "dimensionality bottleneck" of calculations that rely on *global* potential energy surfaces, see for instance the discussion on p. 420 in Ref. 109.

What is needed in *ab initio* molecular dynamics instead? Suppose that a useful trajectory consists of about 10^M molecular dynamics steps, i.e. 10^M electronic structure calculations are needed to generate one trajectory. Furthermore, it is assumed that 10^n independent trajectories are necessary in order to average over different initial conditions so that 10^{M+n} *ab initio* molecular dynamics steps are required in total. Finally, it is assumed that each single–point electronic structure calculation needed to devise the global potential energy surface and one *ab initio* molecular dynamics time step requires roughly the same amount of CPU time. Based on this truly simplistic order of magnitude estimate,

the advantage of *ab initio* molecular dynamics vs. calculations relying on the computation of a global potential energy surface amounts to about $10^{3N-6-M-n}$. The crucial point is that for a given statistical accuracy (that is for M and n fixed and independent of N) and for a given electronic structure method, the computational advantage of "on–the–fly" approaches grows like $\sim 10^N$ with system size.

Of course, considerable progress has been achieved in trajectory calculations by carefully selecting the discretization points and reducing their number, choosing sophisticated representations and internal coordinates, exploiting symmetry etc. but basically the scaling $\sim 10^N$ with the number of nuclei remains a problem. Other strategies consist for instance in reducing the number of active degrees of freedom by constraining certain internal coordinates, representing less important ones by a (harmonic) bath or friction, or building up the global potential energy surface in terms of few–body fragments. All these approaches, however, invoke approximations beyond the ones of the electronic structure method itself. Finally, it is evident that the computational advantage of the "on–the–fly" approaches diminish as more and more trajectories are needed for a given (small) system. For instance extensive averaging over many different initial conditions is required in order to calculate quantitatively scattering or reactive cross sections. Summarizing this discussion, it can be concluded that *ab initio* molecular dynamics is the method of choice to investigate large and "chemically complex" systems.

A host of review articles dealing with *ab initio* molecular dynamics appeared since the early nineties[222, 91, 201, 193, 92, 59, 265, 97, 195, 225, 178, 179, 268, 161, 112, 87, 181, 180, 142, 6] and the interested reader is referred to them for a variety of complementary viewpoints. The present introduction into the basic methodology is a more focussed and updated version of the Lecture Notes[179] "Ab Initio Molecular Dynamics: Theory and Implementation" with special emphasis on the versatile `CPMD` program package[139] going back to the *NIC Winter School 2000* on "Modern Methods and Algorithms of Quantum Chemistry". The present Notes are intended to establish the basis for more specialized Lectures during the *NIC Winter School 2006* "Computational Nanoscience: Do it Yourself!". The presentation starts from the Schrödinger equation. Classical, Ehrenfest, Born–Oppenheimer, and Car–Parrinello molecular dynamics are "derived" from the time–dependent mean–field approach that is obtained after separating the nuclear and electronic degrees of freedom. The most extensive discussion is related to the features of the basic Car–Parrinello approach but all three *ab initio* approaches to molecular dynamics are contrasted and partly compared. The important issue of how to obtain the correct forces in these schemes is discussed in some depth. The most popular electronic structure theories implemented within *ab initio* molecular dynamics, density functional theory in the first place but also the Hartree–Fock approach, are sketched. Some attention is also given to another important ingredient in *ab initio* molecular dynamics, the choice of the basis set. In addition to the `CPMD` package[139] an *increasing* number of other powerful codes able to perform *ab initio* molecular dynamics simulations is available today (for instance `ABINIT`[1], `CASTEP`[42], `CP-PAW`[52], `CP2k`[51], `Dacapo`[54], `fhi98md`[77], `NWChem`[189], `PINY`[213], `PWscf`/`Quantum-ESPRESSO`[218], `S/PHI/nX`[240], or `VASP`[278] among others) which are partly based on very similar techniques as those discussed here.

2 Theoretical Foundations

2.1 Deriving Classical Molecular Dynamics

The starting point of the following discussion is non–relativistic quantum mechanics as formalized via the time–dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Phi(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t) = \mathcal{H}\Phi(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t) \tag{1}$$

in its position representation in conjunction with the standard Hamiltonian

$$\begin{aligned}\mathcal{H} &= -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 - \sum_i \frac{\hbar^2}{2m_\mathrm{e}}\nabla_i^2 + \sum_{i<j}\frac{\mathrm{e}^2}{|\mathbf{r}_i-\mathbf{r}_j|} - \sum_{I,i}\frac{\mathrm{e}^2 Z_I}{|\mathbf{R}_I-\mathbf{r}_i|} + \sum_{I<J}\frac{\mathrm{e}^2 Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|} \\ &= -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 - \sum_i \frac{\hbar^2}{2m_\mathrm{e}}\nabla_i^2 + V_{\mathrm{n-e}}(\{\mathbf{r}_i\},\{\mathbf{R}_I\}) \\ &= -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \mathcal{H}_\mathrm{e}(\{\mathbf{r}_i\},\{\mathbf{R}_I\})\end{aligned} \tag{2}$$

for the electronic $\{\mathbf{r}_i\}$ and nuclear $\{\mathbf{R}_I\}$ degrees of freedom. The more convenient atomic units (a.u.) will be introduced at a later stage for reasons that will soon become clear. Thus, only the bare electron–electron, electron–nuclear, and nuclear–nuclear Coulomb interactions are taken into account.

The goal of this section is to derive classical molecular dynamics[4, 118, 88, 220] starting from Schrödinger's wave equation and following the elegant route of Tully[271, 272]. To this end, the nuclear and electronic contributions to the total wave function $\Phi(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t)$, which depends on *both* the nuclear and electronic coordinates, *have* to be separated. The simplest possible form is a product ansatz

$$\Phi(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t) \approx \Psi(\{\mathbf{r}_i\};t)\;\chi(\{\mathbf{R}_I\};t)\;\exp\left[\frac{i}{\hbar}\int_{t_0}^{t} dt'\tilde{E}_\mathrm{e}(t')\right] \quad , \tag{3}$$

where the nuclear and electronic wave functions are separately normalized to unity at every instant of time, i.e. $\langle\chi;t|\chi;t\rangle = 1$ and $\langle\Psi;t|\Psi;t\rangle = 1$, respectively. In addition, a convenient phase factor

$$\tilde{E}_\mathrm{e} = \int d\mathbf{r}d\mathbf{R}\;\;\Psi^\star(\{\mathbf{r}_i\};t)\;\chi^\star(\{\mathbf{R}_I\};t)\;\mathcal{H}_\mathrm{e}\;\Psi(\{\mathbf{r}_i\};t)\;\chi(\{\mathbf{R}_I\};t) \tag{4}$$

was introduced at this stage such that the final equations will look nice; $\int d\mathbf{r}d\mathbf{R}$ refers to the integration over all $i = 1,\ldots$ and $I = 1,\ldots$ variables $\{\mathbf{r}_i\}$ and $\{\mathbf{R}_I\}$, respectively. It is mentioned in passing that this approximation is called a one–determinant or single–configuration ansatz for the *total* wave function, which at the end must lead to a mean–field description of the coupled dynamics. Note also that this product ansatz (excluding the phase factor) differs from the Born–Oppenheimer ansatz[155, 162, 65] for separating the fast and slow variables

$$\Phi_\mathrm{BO}(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t) = \sum_{k=0}^{\infty}\tilde{\Psi}_k(\{\mathbf{r}_i\},\{\mathbf{R}_I\})\tilde{\chi}_k(\{\mathbf{R}_I\};t) \tag{5}$$

even in its one–determinant limit, where only a single electronic state k (evaluated for the nuclear configuration $\{\mathbf{R}_I\}$) is included in the expansion.

Inserting the separation ansatz Eq. (3) into Eqs. (1)–(2) yields (after multiplying from the left by $\langle\Psi|$ and $\langle\chi|$ and imposing energy conservation $d\langle\mathcal{H}\rangle/dt \equiv 0$) the following relations

$$i\hbar\frac{\partial\Psi}{\partial t} = -\sum_i \frac{\hbar^2}{2m_\mathrm{e}}\nabla_i^2\Psi + \left\{\int d\mathbf{R}\,\chi^\star(\{\mathbf{R}_I\};t)V_{\mathrm{n-e}}(\{\mathbf{r}_i\},\{\mathbf{R}_I\})\chi(\{\mathbf{R}_I\};t)\right\}\Psi \quad (6)$$

$$i\hbar\frac{\partial\chi}{\partial t} = -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2\chi + \left\{\int d\mathbf{r}\;\Psi^\star(\{\mathbf{r}_i\};t)\mathcal{H}_\mathrm{e}(\{\mathbf{r}_i\},\{\mathbf{R}_I\})\Psi(\{\mathbf{r}_i\};t)\right\}\chi\ . \quad (7)$$

This set of coupled equations defines the basis of the time–dependent self–consistent field (TDSCF) method introduced as early as 1930 by Dirac[62], see also Ref. 59. Both electrons and nuclei move quantum–mechanically in time–dependent effective potentials (or self–consistently obtained average fields) obtained from appropriate averages (quantum mechanical expectation values $\langle\ldots\rangle$) over the other class of degrees of freedom (by using the nuclear and electronic wave functions, respectively). Thus, the single–determinant ansatz Eq. (3) produces, as already anticipated, a mean–field description of the coupled nuclear–electronic quantum dynamics. This is the price to pay for the simplest possible separation of electronic and nuclear variables.

The next step in the derivation of classical molecular dynamics is the task to approximate the nuclei as classical point particles. How can this be achieved in the framework of the TDSCF approach, given one quantum–mechanical wave equation describing all nuclei? A well–known route to extract classical mechanics from quantum mechanics in general starts with rewriting the corresponding wave function

$$\chi(\{\mathbf{R}_I\};t) = A(\{\mathbf{R}_I\};t)\,\exp\left[iS(\{\mathbf{R}_I\};t)/\hbar\right] \quad (8)$$

in terms of an amplitude factor A and a phase S which are both considered to be real and $A > 0$ in this polar representation, see for instance Refs. 63, 184, 224. After transforming the nuclear wave function in Eq. (7) accordingly and after separating the real and imaginary parts, the TDSCF equation for the nuclei

$$\frac{\partial S}{\partial t} + \sum_I \frac{1}{2M_I}\left(\nabla_I S\right)^2 + \int d\mathbf{r}\;\Psi^\star\mathcal{H}_\mathrm{e}\Psi = \hbar^2\sum_I \frac{1}{2M_I}\frac{\nabla_I^2 A}{A} \quad (9)$$

$$\frac{\partial A}{\partial t} + \sum_I \frac{1}{M_I}\left(\nabla_I A\right)\left(\nabla_I S\right) + \sum_I \frac{1}{2M_I}A\left(\nabla_I^2 S\right) = 0 \quad (10)$$

is (exactly) re–expressed in terms of the new variables A and S. This so–called "quantum fluid dynamical representation" Eqs. (9)–(10) can actually be used to solve the time–dependent Schrödinger equation[61]. The relation for A, Eq. (10), can be rewritten as a continuity equation[63, 184, 224] with the help of the identification of the nuclear density $|\chi|^2 \equiv A^2$ as directly obtained from the definition Eq. (8). This continuity equation is independent of $\hbar$ and ensures locally the conservation of the particle probability $|\chi|^2$ associated to the nuclei in the presence of a flux.

More important for the present purpose is a more detailed discussion of the relation for S, Eq. (9). This equation contains one term that depends on $\hbar$, a contribution that vanishes

if the classical limit

$$\frac{\partial S}{\partial t} + \sum_I \frac{1}{2M_I} \left(\nabla_I S\right)^2 + \int d\mathbf{r}\ \Psi^\star \mathcal{H}_\mathrm{e} \Psi = 0 \tag{11}$$

is taken as $\hbar \to 0$; an expansion in terms of $\hbar$ would lead to a hierarchy of semiclassical methods[184, 111]. The resulting equation is now isomorphic to equations of motion in the Hamilton–Jacobi formulation[104, 227]

$$\frac{\partial S}{\partial t} + \mathcal{H}\left(\{\mathbf{R}_I\}, \{\nabla_I S\}\right) = 0 \tag{12}$$

of classical mechanics with the classical Hamilton function

$$\mathcal{H}(\{\mathbf{R}_I\}, \{\mathbf{P}_I\}) = T(\{\mathbf{P}_I\}) + V(\{\mathbf{R}_I\}) \tag{13}$$

defined in terms of (generalized) coordinates $\{\mathbf{R}_I\}$ and their conjugate momenta $\{\mathbf{P}_I\}$. With the help of the connecting transformation

$$\mathbf{P}_I \equiv \nabla_I S \tag{14}$$

the Newtonian equation of motion $\dot{\mathbf{P}}_I = -\nabla_I V(\{\mathbf{R}_I\})$ corresponding to Eq. (11)

$$\begin{aligned} \frac{d\mathbf{P}_I}{dt} &= -\nabla_I \int d\mathbf{r}\ \Psi^\star \mathcal{H}_\mathrm{e} \Psi \qquad \text{or} \\ M_I \ddot{\mathbf{R}}_I(t) &= -\nabla_I \int d\mathbf{r}\ \Psi^\star \mathcal{H}_\mathrm{e} \Psi \qquad (15) \\ &= -\nabla_I V_\mathrm{e}^\mathrm{E}(\{\mathbf{R}_I(t)\}) \qquad (16) \end{aligned}$$

can be read off. Thus, the nuclei move according to classical mechanics in an effective potential V_e^E due to the electrons. This potential is a function of only the nuclear positions at time t as a result of averaging $\mathcal{H}_\mathrm{e}$ over the electronic degrees of freedom, i.e. computing its quantum expectation value $\langle \Psi | \mathcal{H}_\mathrm{e} | \Psi \rangle$, while keeping the nuclear positions fixed at their instantaneous values $\{\mathbf{R}_I(t)\}$.

However, the nuclear wave function still occurs in the TDSCF equation for the electronic degrees of freedom and has to be replaced by the positions of the nuclei for consistency. In this case the classical reduction can be achieved simply by replacing the nuclear density $|\chi(\{\mathbf{R}_I\}; t)|^2$ in Eq. (6) in the limit $\hbar \to 0$ by a product of delta functions $\prod_I \delta(\mathbf{R}_I - \mathbf{R}_I(t))$ centered at the instantaneous positions $\{\mathbf{R}_I(t)\}$ of the classical nuclei as given by Eq. (15). This yields e.g. for the position operator

$$\int d\mathbf{R}\ \chi^\star(\{\mathbf{R}_I\}; t)\ \mathbf{R}_I\ \chi(\{\mathbf{R}_I\}; t) \ \stackrel{\hbar \to 0}{\longrightarrow}\ \mathbf{R}_I(t) \tag{17}$$

the required expectation value. This classical limit leads to a time–dependent wave equation for the electrons

$$\begin{aligned} i\hbar \frac{\partial \Psi}{\partial t} &= -\sum_i \frac{\hbar^2}{2m_\mathrm{e}} \nabla_i^2 \Psi + V_{\mathrm{n-e}}(\{\mathbf{r}_i\}, \{\mathbf{R}_I(t)\}) \Psi \\ &= \mathcal{H}_\mathrm{e}(\{\mathbf{r}_i\}, \{\mathbf{R}_I(t)\})\ \ \Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t) \end{aligned} \tag{18}$$

which evolve self–consistently as the classical nuclei are propagated via Eq. (15). Note that now $\mathcal{H}_\mathrm{e}$ and thus Ψ depend *parametrically* on the classical nuclear *positions* $\{\mathbf{R}_I(t)\}$

at time t through $V_{\mathrm{n-e}}(\{\mathbf{r}_i\},\{\mathbf{R}_I(t)\})$. This means that feedback between the classical and quantum degrees of freedom is incorporated in both directions (at variance with the "classical path" or Mott non–SCF approach to dynamics[271,272]).

The approach relying on solving Eq. (15) together with Eq. (18) is sometimes called "Ehrenfest molecular dynamics" in honor of Ehrenfest who was the first to address the question [a] of how Newtonian classical dynamics can be derived from Schrödinger's wave equation[69]. In the present case this leads to a hybrid or mixed approach because only the nuclei are forced to behave like classical particles, whereas the electrons are still treated as quantum objects.

Although the TDSCF approach underlying Ehrenfest molecular dynamics clearly is a mean–field theory, transitions between electronic states are included in this scheme. This can be made evident by expanding the *electronic* wave function Ψ (as opposed to the *total* wave function Φ according to Eq. (5)) in terms of many electronic states or determinants Ψ_k

$$\Psi(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t)=\sum_{k=0}^{\infty}c_k(t)\Psi_k(\{\mathbf{r}_i\};\{\mathbf{R}_I\}) \tag{19}$$

with complex coefficients $\{c_k(t)\}$. In this case, the coefficients $\{|c_k(t)|^2\}$ (with $\sum_k |c_k(t)|^2 \equiv 1$) describe explicitly the time evolution of the populations (occupations) of the different states $\{k\}$ whereas interferences are included via the $\{c_k^\star c_{l\neq k}\}$ contributions. One possible choice for the basis functions $\{\Psi_k\}$ is the adiabatic basis obtained from solving the time–independent electronic Schrödinger equation

$$\mathcal{H}_{\mathrm{e}}(\{\mathbf{r}_i\};\{\mathbf{R}_I\})\Psi_k=E_k(\{\mathbf{R}_I\})\Psi_k(\{\mathbf{r}_i\};\{\mathbf{R}_I\}) \ , \tag{20}$$

where $\{\mathbf{R}_I\}$ are the instantaneous nuclear positions at time t according to Eq. (15). The actual equations of motion in terms of the expansion coefficients $\{c_k\}$ are presented in Section 2.2.

At this stage a further simplification can be invoked by restricting the total electronic wave function Ψ to be the ground state wave function Ψ_0 of $\mathcal{H}_{\mathrm{e}}$ at each instant of time according to Eq. (20) and $|c_0(t)|^2 \equiv 1$ in Eq. (19). This should be a good approximation if the energy difference between Ψ_0 and the first excited state Ψ_1 is everywhere large compared to the thermal energy $k_{\mathrm{B}}T$, roughly speaking. In this limit the nuclei move according to Eq. (15) on a single potential energy surface

$$V_{\mathrm{e}}^{\mathrm{E}}=\int d\mathbf{r}\ \Psi_0^\star\mathcal{H}_{\mathrm{e}}\Psi_0 \equiv E_0(\{\mathbf{R}_I\}) \tag{21}$$

that can be computed by solving the *time–independent* electronic Schrödinger equation Eq. (20)

$$\mathcal{H}_{\mathrm{e}}\Psi_0=E_0\Psi_0 \ , \tag{22}$$

for the ground state only. This leads to the identification $V_{\mathrm{e}}^{\mathrm{E}} \equiv E_0$ via Eq. (21), i.e. in this limit the Ehrenfest potential is identical to the ground–state Born–Oppenheimer potential.

[a] The opening statement of Ehrenfest's famous 1927 paper[69] reads:
"Es ist wünschenswert, die folgende Frage möglichst elementar beantworten zu können: *Welcher Rückblick ergibt sich vom Standpunkt der Quantenmechanik auf die Newtonschen Grundgleichungen der klassischen Mechanik?"*

As a consequence of this observation, it is conceivable to decouple the task of generating the nuclear dynamics from the task of computing the potential energy surface. In a first step E_0 is computed for many nuclear configurations by solving Eq. (22). In a second step, these data points are fitted to an analytical functional form to yield a global potential energy surface[226], from which the gradients can be obtained analytically. In a third step, the Newtonian equation of motion Eq. (16) is solved on this surface for many different initial conditions, producing a "swarm" of classical trajectories. This is, in a nutshell, the basis of *classical trajectory calculations* on global potential energy surfaces[270, 228].

As already alluded to in the general introduction, such approaches suffer severely from the "dimensionality bottleneck" as the number of active nuclear degrees of freedom increases. One traditional way out of this dilemma is to approximate the global potential energy surface

$$V_{\mathrm{e}}^{\mathrm{E}} \approx V_{\mathrm{e}}^{\mathrm{approx}}(\{\mathbf{R}_I\}) = \sum_{I=1}^{N} v_1(\mathbf{R}_I) + \sum_{I<J}^{N} v_2(\mathbf{R}_I, \mathbf{R}_J) + \sum_{I<J<K}^{N} v_3(\mathbf{R}_I, \mathbf{R}_J, \mathbf{R}_K) + \cdots \tag{23}$$

in terms of a truncated expansion of many–body contributions[108, 4, 118]. At this stage, the electronic degrees of freedom are replaced by interaction potentials $\{v_n\}$ and are not featured as explicit degrees of freedom in the equations of motion. Thus, the mixed quantum / classical problem is reduced to purely classical mechanics, once the $\{v_n\}$ are determined. *Classical molecular dynamics*

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I V_{\mathrm{e}}^{\mathrm{approx}}(\{\mathbf{R}_I(t)\}) \tag{24}$$

relies crucially on this idea, where typically only two–body v_2 or three–body v_3 interactions are taken into account[4, 118], although more sophisticated models to include non–additive interactions such as polarization exist. This amounts to a dramatic simplification and removes the dimensionality bottleneck as the global potential surface is constructed from a manageable sum of additive few–body contributions — at the price of introducing a drastic approximation and of basically excluding chemical transformations from the realm of simulations.

As a result of this derivation, the essential assumptions underlying classical molecular dynamics become transparent: the electrons follow adiabatically the classical nuclear motion and can be integrated out so that the nuclei evolve on a single Born–Oppenheimer potential energy surface (typically but not necessarily given by the electronic ground state), which is in general approximated in terms of few–body interactions.

Actually, classical molecular dynamics for *many*–body systems is only made possible by somehow decomposing the global potential energy. In order to illustrate this point consider the simulation of $N = 500$ Argon atoms in the liquid phase[70] where the interactions can faithfully be described by additive two–body terms, i.e. $V_{\mathrm{e}}^{\mathrm{approx}}(\{\mathbf{R}_I\}) \approx \sum_{I<J}^{N} v_2(|\mathbf{R}_I - \mathbf{R}_J|)$. Thus, the determination of the pair potential v_2 from *ab initio* electronic structure calculations amounts to computing and fitting a one–dimensional function. The corresponding task to determine a global potential energy surface amounts to doing that in about 10^{1500} dimensions, which is simply impossible (and on top of that not necessary for Nobel gases!).

2.2 Ehrenfest Molecular Dynamics

A way out of the dimensionality bottleneck other than to approximate the global potential energy surface Eq. (23) or to reduce the number of active degrees of freedom is to take seriously the classical nuclei approximation to the TDSCF equations, Eqs. (15) and (18). This amounts to computing the Ehrenfest force by actually solving numerically

$$\begin{aligned} M_I \ddot{\mathbf{R}}_I(t) &= -\nabla_I \int d\mathbf{r}\; \Psi^\star \mathcal{H}_\mathrm{e} \Psi \\ &= -\nabla_I \left\langle \Psi \left| \mathcal{H}_\mathrm{e} \right| \Psi \right\rangle \\ &= -\nabla_I \left\langle \mathcal{H}_\mathrm{e} \right\rangle \\ &= -\nabla_I V_\mathrm{e}^\mathrm{E} \end{aligned} \tag{25}$$

$$\begin{aligned} i\hbar \frac{\partial \Psi}{\partial t} &= \left[-\sum_i \frac{\hbar^2}{2m_\mathrm{e}} \nabla_i^2 + V_{\mathrm{n-e}}(\{\mathbf{r}_i\}, \{\mathbf{R}_I(t)\}) \right] \Psi \\ &= \mathcal{H}_\mathrm{e} \Psi \end{aligned} \tag{26}$$

the coupled set of equations simultaneously. Thereby, the *a priori* construction of any type of potential energy surface is avoided from the outset by solving the time–dependent electronic Schrödinger equation "on–the–fly". This allows one to compute the force from $\nabla_I \langle \mathcal{H}_\mathrm{e} \rangle$ for each configuration $\{\mathbf{R}_I(t)\}$ generated by molecular dynamics; see Section 2.5 for the issue of using the so–called "Hellmann–Feynman forces" instead.

The corresponding equations of motion in terms of the adiabatic basis Eq. (20) and the time–dependent expansion coefficients Eq. (19) read[271, 272, 65]

$$M_I \ddot{\mathbf{R}}_I(t) = -\sum_k |c_k(t)|^2 \nabla_I E_k - \sum_{k,l} c_k^\star c_l \left(E_k - E_l\right) \mathbf{d}_I^{kl} \tag{27}$$

$$i\hbar \dot{c}_k(t) = c_k(t) E_k - i\hbar \sum_{I,l} c_l(t) \dot{\mathbf{R}}_I \mathbf{d}_I^{kl} \quad , \tag{28}$$

where the coupling terms are given by

$$\mathbf{d}_I^{kl}(\{\mathbf{R}_I(t)\}) = \int d\mathbf{r}\; \Psi_k^\star \nabla_I \Psi_l \tag{29}$$

with the property $\mathbf{d}_I^{kk} \equiv \mathbf{0}$. The Ehrenfest approach is thus seen to include rigorously non–adiabatic transitions between different electronic states Ψ_k and Ψ_l within the framework of classical nuclear motion and the *mean–field* (TDSCF) approximation to the electronic structure, see e.g. Refs. 271, 272, 65 for reviews and for instance Ref. 223 for an implementation in terms of time–dependent density functional theory.

The restriction to one electronic state in the expansion Eq. (19), which is in most cases the ground state Ψ_0, leads to

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \left\langle \Psi_0 \left| \mathcal{H}_\mathrm{e} \right| \Psi_0 \right\rangle \tag{30}$$

$$i\hbar \frac{\partial \Psi_0}{\partial t} = \mathcal{H}_\mathrm{e} \Psi_0 \tag{31}$$

as a special case of Eqs. (25)–(26); note that $\mathcal{H}_\mathrm{e}$ is time–dependent via the nuclear coordinates $\{\mathbf{R}_I(t)\}$. A point worth mentioning here is that the propagation of the wave function

is unitary, i.e. the wave function preserves its norm and the set of orbitals used to build up the wave function will stay orthonormal, see Section 2.6.

Ehrenfest molecular dynamics is certainly the oldest approach to "on–the–fly" molecular dynamics and is typically used for collision– and scattering–type problems[55, 270, 185, 56]. Traditionally, the Ehrenfest approach to electron dynamics has not been in widespread use for systems with many active degrees of freedom typical for condensed matter problems. More recently, however, its usage in conjunction with time–dependent density functional theory to describe the electronic subsystem gained a lot of attention, see e.g. Refs. 233, 12, 83, 258, 223, 24, 25, 251 for various such implementations.

2.3 Born–Oppenheimer Molecular Dynamics

An alternative approach to include the electronic structure in molecular dynamics simulations consists in straightforwardly solving the *static* electronic structure problem in each molecular dynamics step given the set of *fixed* nuclear positions at that instance of time. Thus, the electronic structure part is reduced to solving a *time–independent* quantum problem, e.g. by solving the time–independent Schrödinger equation, concurrently to propagating the nuclei via classical molecular dynamics. Thus, the time–dependence of the electronic structure is a consequence of nuclear motion, and not intrinsic as in Ehrenfest molecular dynamics. The resulting Born–Oppenheimer molecular dynamics method is defined by

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \min_{\Psi_0} \{\langle \Psi_0 | \mathcal{H}_\mathrm{e} | \Psi_0 \rangle\} \tag{32}$$

$$E_0 \Psi_0 = \mathcal{H}_\mathrm{e} \Psi_0 \tag{33}$$

for the electronic ground state. A deep difference with respect to Ehrenfest dynamics concerning the nuclear equation of motion is that the minimum of $\langle \mathcal{H}_\mathrm{e} \rangle$ has to be reached in each Born–Oppenheimer molecular dynamics step according to Eq. (32). In Ehrenfest dynamics, on the other hand, a wave function that minimized $\langle \mathcal{H}_\mathrm{e} \rangle$ initially will also stay in its respective minimum as the nuclei move according to Eq. (30)!

A natural and straightforward extension[125] of ground–state Born–Oppenheimer dynamics is to apply the same scheme to any excited electronic state Ψ_k without considering any interferences. In particular, this means that also the "diagonal correction terms"[155]

$$D_I^{kk}(\{\mathbf{R}_I(t)\}) = -\int d\mathbf{r}\ \Psi_k^\star \nabla_I^2 \Psi_k \tag{34}$$

are *always* neglected; the inclusion of such terms is discussed for instance in Refs. 271,272. These terms renormalize the Born–Oppenheimer or "clamped nuclei" potential energy surface E_k of a given state Ψ_k (which might also be the ground state Ψ_0) and lead to the so–called "adiabatic potential energy surface" of that state[155]. Whence, Born–Oppenheimer molecular dynamics should not be called "adiabatic molecular dynamics", as is sometime done.

It is useful for the sake of later reference to formulate the Born–Oppenheimer equations of motion for the special case of effective one–particle Hamiltonians. This might be the Hartree–Fock approximation defined to be the variational minimum of the energy expectation value $\langle \Psi_0 | \mathcal{H}_\mathrm{e} | \Psi_0 \rangle$ given a single Slater determinant $\Psi_0 = \det\{\psi_i\}$ subject

to the constraint that the one–particle orbitals ψ_i are orthonormal $\langle \psi_i \,|\psi_j \rangle = \delta_{ij}$. The corresponding constraint minimization of the total energy with respect to the orbitals

$$\min_{\{\psi_i\}} \{ \langle \Psi_0 \,|\mathcal{H}_\mathrm{e}|\, \Psi_0 \rangle \} \Big|_{\{\langle \psi_i | \psi_j \rangle = \delta_{ij}\}} \tag{35}$$

can be cast into Lagrange's formalism

$$\mathcal{L} = -\langle \Psi_0 \,|\mathcal{H}_\mathrm{e}|\, \Psi_0 \rangle + \sum_{i,j} \Lambda_{ij} \left(\langle \psi_i \,|\psi_j \rangle - \delta_{ij} \right) \tag{36}$$

where Λ_{ij} are the associated Lagrangian multipliers. Unconstrained variation of this Lagrangian with respect to the orbitals

$$\frac{\delta \mathcal{L}}{\delta \psi_i^\star} \stackrel{!}{=} 0 \tag{37}$$

leads to the well–known Hartree–Fock equations

$$\mathcal{H}_\mathrm{e}^\mathrm{HF} \psi_i = \sum_j \Lambda_{ij} \psi_j \tag{38}$$

as derived in standard text books[252,183]; the diagonal canonical form $\mathcal{H}_\mathrm{e}^\mathrm{HF} \psi_i = \epsilon_i \psi_i$ is obtained after a unitary transformation and $\mathcal{H}_\mathrm{e}^\mathrm{HF}$ denotes the effective one–particle Hamiltonian, see Section 2.7 for more details. The equations of motion corresponding to Eqs. (32)–(33) read

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \min_{\{\psi_i\}} \left\{ \left\langle \Psi_0 \left| \mathcal{H}_\mathrm{e}^\mathrm{HF} \right| \Psi_0 \right\rangle \right\} \tag{39}$$

$$0 = -\mathcal{H}_\mathrm{e}^\mathrm{HF} \psi_i + \sum_j \Lambda_{ij} \psi_j \tag{40}$$

for the Hartree–Fock case. A similar set of equations is obtained if Hohenberg–Kohn–Sham density functional theory[194,66,176] is used, where $\mathcal{H}_\mathrm{e}^\mathrm{HF}$ has to be replaced by the Kohn–Sham effective one–particle Hamiltonian H_e^KS, see Section 2.7 for more details. Instead of diagonalizing the one–particle Hamiltonian an alternative but equivalent approach consists in directly performing the constraint minimization according to Eq. (35) via non-linear optimization techniques.

Early applications of Born–Oppenheimer molecular dynamics were performed in the framework of a semiempirical approximation to the electronic structure problem[281,282]. But only a few years later an *ab initio* approach was implemented within the Hartree–Fock approximation[166]. Born–Oppenheimer dynamics started to become popular in the early nineties with the availability of more efficient electronic structure codes in conjunction with sufficient computer power to solve "interesting problems", see for instance the compilation of such studies in Table 1 in a recent overview article[32]. More recently, a revival of these activities with greatly improved algorithms to perform Born–Oppenheimer simulations is observed[278,159,160,277,137].

Undoubtedly, the breakthrough of Hohenberg–Kohn–Sham density functional theory in the realm of chemistry – which took place around the same time – also helped a lot by greatly improving the "price / performance ratio" of the electronic structure part, see e.g. Refs. 289, 246, 188. A third and possibly the crucial reason that boosted the field of *ab initio* molecular dynamics was the pioneering introduction of the Car–Parrinello approach[38],

see also Figure 1. This technique opened novel avenues to treat large–scale problems via *ab initio* molecular dynamics and catalyzed the entire field by making "interesting calculations" possible, see also the closing section on applications.

2.4 Car–Parrinello Molecular Dynamics

2.4.1 Motivation

A non–obvious approach to cut down the computational expenses of molecular dynamics which includes the electrons in a single state was proposed by Car and Parrinello in 1985[38]. In retrospect it can be considered to combine the advantages of both Ehrenfest and Born–Oppenheimer molecular dynamics. In Ehrenfest dynamics the time scale and thus the time step to integrate Eqs. (30) and (31) simultaneously is dictated by the intrinsic dynamics of the electrons. Since electronic motion is much faster than nuclear motion, the largest possible time step is that which allows to integrate the electronic equations of motion. Contrary to that, there is no electron dynamics whatsoever involved in solving the Born–Oppenheimer Eqs. (32)–(33), i.e. they can be integrated on the time scale given by nuclear motion. However, this means that the electronic structure problem has to be solved self–consistently at each molecular dynamics step, whereas this is avoided in Ehrenfest dynamics due to the possibility to propagate the wave function by applying the Hamiltonian to an initial wave function (obtained e.g. by one self–consistent diagonalization).

From an algorithmic point of view the main task achieved in ground–state Ehrenfest dynamics is simply to keep the wave function automatically minimized as the nuclei are propagated. This, however, might be achieved – in principle – by another sort of deterministic dynamics than first–order Schrödinger dynamics. In summary, the "Best of all Worlds Method" should (i) integrate the equations of motion on the (long) time scale set by the nuclear motion but nevertheless (ii) take intrinsically advantage of the smooth time–evolution of the dynamically evolving electronic subsystem as much as possible. The second point allows to circumvent explicit diagonalization or minimization to solve the electronic structure problem for the next molecular dynamics step. Car–Parrinello molecular dynamics is an efficient method to satisfy requirement (ii) in a numerically stable fashion and makes an acceptable compromise concerning the length of the time step (i).

2.4.2 Car–Parrinello Lagrangian and Equations of Motion

The basic idea of the Car–Parrinello approach can be viewed to exploit the quantum–mechanical adiabatic time–scale separation of fast electronic and slow nuclear motion by transforming that into classical–mechanical adiabatic energy–scale separation in the framework of dynamical systems theory. In order to achieve this goal the two–component quantum / classical problem is mapped onto a two–component purely classical problem with two separate energy scales at the expense of loosing the explicit time–dependence of the quantum subsystem dynamics. Furthermore, the central quantity, the energy of the electronic subsystem $\langle \Psi_0 | \mathcal{H}_\mathrm{e} | \Psi_0 \rangle$ evaluated with some wave function Ψ_0, is certainly a function of the nuclear positions $\{\mathbf{R}_I\}$. But at the same time it *can* be considered to be a functional of the wave function Ψ_0 and thus of a set of one–particle orbitals $\{\psi_i\}$ (or in general of other functions such as two–particle geminals) used to build up this wave function (being for instance a Slater determinant $\Psi_0 = \det\{\psi_i\}$ or a combination thereof).

Now, in classical mechanics the force on the nuclei is obtained from the derivative of a Lagrangian with respect to the nuclear positions. This suggests that a functional derivative with respect to the orbitals, which are interpreted as classical fields, might yield the force on the orbitals, given a suitable Lagrangian. In addition, possible constraints within the set of orbitals have to be imposed, such as e.g. orthonormality (or generalized orthonormality conditions that include an overlap matrix).

Car and Parrinello postulated the following class of Lagrangians[38]

$$\mathcal{L}_{\mathrm{CP}} = \underbrace{\sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \mu \left\langle \dot{\psi}_i \middle| \dot{\psi}_i \right\rangle}_{\text{kinetic energy}} - \underbrace{\langle \Psi_0 | \mathcal{H}_{\mathrm{e}} | \Psi_0 \rangle}_{\text{potential energy}} + \underbrace{\textit{constraints}}_{\text{orthonormality}} \tag{41}$$

to serve this purpose; note that sometimes the prefactor $\mu_i/2$ is used and orbital occupation numbers $f_i = 0, 1, 2$ are introduced. The corresponding Newtonian equations of motion are obtained from the associated Euler–Lagrange equations

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I} \tag{42}$$

$$\frac{d}{dt} \frac{\delta \mathcal{L}}{\delta \dot{\psi}_i^\star} = \frac{\delta \mathcal{L}}{\delta \psi_i^\star} \tag{43}$$

like in classical mechanics, but here for both the nuclear positions and the orbitals; note $\psi_i^\star = \langle \psi_i |$ and that the constraints are holonomic[104]. Following this route of ideas, generic Car–Parrinello equations of motion are found to be of the form

$$M_I \ddot{\mathbf{R}}_I(t) = -\frac{\partial}{\partial \mathbf{R}_I} \langle \Psi_0 | \mathcal{H}_{\mathrm{e}} | \Psi_0 \rangle + \frac{\partial}{\partial \mathbf{R}_I} \{\textit{constraints}\} \tag{44}$$

$$\mu \ddot{\psi}_i(t) = -\frac{\delta}{\delta \psi_i^\star} \langle \Psi_0 | \mathcal{H}_{\mathrm{e}} | \Psi_0 \rangle + \frac{\delta}{\delta \psi_i^\star} \{\textit{constraints}\} \tag{45}$$

where μ are the "fictitious masses" or inertia parameters assigned to the orbital degrees of freedom; the units of the mass parameter μ are energy times a squared time for reasons of dimensionality. Note that the constraints within the total wave function lead to "constraint forces" in the equations of motion. Note also that these constraints

$$\textit{constraints} = \textit{constraints} \;\; (\{\psi_i\}, \{\mathbf{R}_I\}) \tag{46}$$

might be a function of both the set of orbitals $\{\psi_i\}$ and the nuclear positions $\{\mathbf{R}_I\}$. These dependencies have to be taken into account properly in deriving the Car–Parrinello equations following from Eq. (41) using Eqs. (42)–(43), see Section 2.5 for a general discussion and see e.g. Ref. 163 for a case with an additional dependence of the wave function constraint on nuclear positions.

According to the Car–Parrinello equations of motion, the nuclei evolve in time at a certain (instantaneous) physical temperature $\propto \sum_I M_I \dot{\mathbf{R}}_I^2$, whereas a "fictitious temperature" $\propto \sum_i \mu \langle \dot{\psi}_i | \dot{\psi}_i \rangle$ is associated to the electronic degrees of freedom. In this terminology, "low electronic temperature" or "cold electrons" means that the electronic subsystem is close to its instantaneous minimum energy $\min_{\{\psi_i\}} \langle \Psi_0 | \mathcal{H}_{\mathrm{e}} | \Psi_0 \rangle$, i.e. close to the exact Born–Oppenheimer surface. Thus, a ground–state wave function optimized for the initial configuration of the nuclei will stay close to its ground state also during time evolution if it is kept at a sufficiently low temperature.

The remaining task is to separate in practice nuclear and electronic motion such that the fast electronic subsystem stays cold also for long times but still follows the slow nuclear motion adiabatically (or instantaneously). Simultaneously, the nuclei are nevertheless kept at a much higher temperature. This can be achieved in nonlinear classical dynamics via decoupling of the two subsystems and (quasi–) adiabatic time evolution. This is possible if the power spectra stemming from both dynamics do not have substantial overlap in the frequency domain so that energy transfer from the "hot nuclei" to the "cold electrons" becomes practically impossible on the relevant time scales. This amounts in other words to imposing and maintaining a metastability condition in a complex dynamical system for sufficiently long times. How and to which extent this is possible in practice was analyzed in detail in a pioneering technical investigation based on well–controlled model systems[197] (see also Refs. 40, 198, 254 and Sects. 3.2 and 3.3 in Ref. 222). Later the adiabaticity issue has been investigated with more mathematical rigor[33] and in terms of a generalization to a second level of adiabatic decoupling[177].

2.4.3 Why Does the Car–Parrinello Method Work ?

In order to shed light on the title question, the dynamics generated by the Car–Parrinello Lagrangian Eq. (41) is analyzed[197] in more detail invoking a "classical dynamics perspective" of a simple model system (eight silicon atoms forming a periodic diamond lattice, local density approximation to density functional theory, normconserving pseudopotentials for core electrons, plane wave basis for valence orbitals, 0.3 fs time step with $\mu = 300$ a.u., in total 20 000 time steps or 6.3 ps), for full details see Ref. 197); a concise presentation of similar ideas can be found in Ref. 40. For this system the vibrational density of states or power spectrum of the electronic degrees of freedom, i.e. the Fourier transform of the statistically averaged velocity autocorrelation function of the classical fields

$$f(\omega) = \int_0^\infty dt \cos(\omega t) \sum_i \left\langle \dot{\psi}_i; t \left| \dot{\psi}_i; 0 \right. \right\rangle \tag{47}$$

is compared to the highest–frequency phonon mode $\omega_{\rm n}^{\rm max}$ of the nuclear subsystem in Figure 2. From this figure it is evident that for the chosen parameters the nuclear and electronic subsystems are dynamically separated: their power spectra do not overlap so that energy transfer from the hot to the cold subsystem is expected to be prohibitively slow, see Section 3.3 in Ref. 222 for a similar argument.

This is indeed the case as can be verified in Figure 3 where the conserved energy $E_{\rm cons}$, physical total energy $E_{\rm phys}$, electronic energy $V_{\rm e}$, and fictitious kinetic energy of the electrons $T_{\rm e}$

$$E_{\rm cons} = \sum_i \mu \left\langle \dot{\psi}_i \left| \dot{\psi}_i \right. \right\rangle + \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \langle \Psi_0 | \mathcal{H}_{\rm e} | \Psi_0 \rangle \tag{48}$$

$$E_{\rm phys} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \langle \Psi_0 | \mathcal{H}_{\rm e} | \Psi_0 \rangle = E_{\rm cons} - T_{\rm e} \tag{49}$$

$$V_{\rm e} = \langle \Psi_0 | \mathcal{H}_{\rm e} | \Psi_0 \rangle \tag{50}$$

$$T_{\rm e} = \sum_i \mu \left\langle \dot{\psi}_i \left| \dot{\psi}_i \right. \right\rangle \tag{51}$$

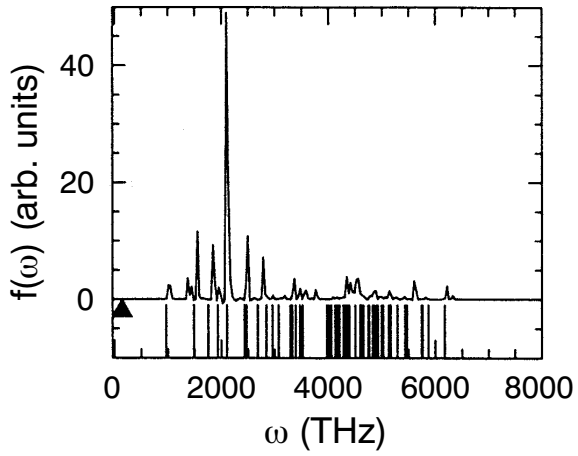

Figure 2. Vibrational density of states Eq. (47) (continuous spectrum in upper part) and harmonic approximation thereof Eq. (52) (stick spectrum in lower part) of the electronic degrees of freedom compared to the highest–frequency phonon mode $\omega_{\mathrm{n}}^{\mathrm{max}}$ (triangle) for a model system; for further details see text. Adapted from Ref. 197.

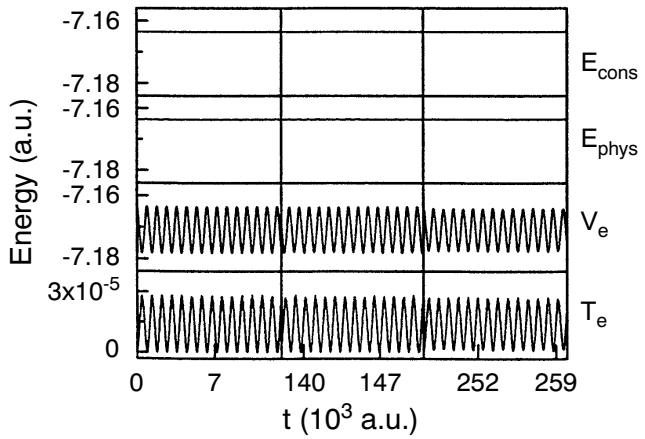

Figure 3. Various energies Eqs. (48)–(51) for a model system propagated via Car–Parrinello molecular dynamics for at short (up to 300 fs), intermediate, and long times (up to 6.3 ps); for further details see text. Adapted from Ref. 197.

are shown for the same system as a function of time. First of all, there should be a conserved energy quantity according to classical dynamics since the constraints are holonomic[104]. Indeed "the Hamiltonian" or conserved energy E_{cons} is a constant of motion (with relative variations smaller than 10^{-6} and with no drift), which serves as an extremely sensitive check of the molecular dynamics algorithm. Contrary to that the electronic energy V_{e} displays a simple oscillation pattern due to the simplicity of the phonon modes.

Most importantly, the fictitious kinetic energy of the electrons T_{e} is found to perform

bound oscillations around a *constant*, i.e. the electrons "do not heat up" systematically in the presence of the hot nuclei; note that T_{e} is a measure for deviations from the exact Born–Oppenheimer surface. Closer inspection shows actually two time scales of oscillations: the one visible in Figure 3 stems from the drag exerted by the moving nuclei on the electrons and is the mirror image of the V_{e} fluctuations. Superimposed on top of that (not shown, but see Figure 4(b)) are small–amplitude high frequency oscillations intrinsic to the fictitious electron dynamics with a period of only a fraction of the visible mode. These oscillations are actually instrumental for the stability of the Car–Parrinello dynamics, vide infra. But already the visible variations are three orders of magnitude smaller than the physically meaningful oscillations of V_{e}. As a result, E_{phys} defined as $E_{\mathrm{cons}} - T_{\mathrm{e}}$ or equivalently as the sum of the nuclear kinetic energy and the electronic total energy (which serves as the potential energy for the nuclei) is essentially constant on the relevant energy and time scales. Thus, it behaves approximately like the strictly conserved total energy in classical molecular dynamics (with only nuclei as dynamical degrees of freedom) or in Born–Oppenheimer molecular dynamics (with fully optimized electronic degrees of freedom) and is therefore often denoted as the "physical total energy". This implies that the resulting physically significant dynamics of the nuclei yields an excellent approximation to microcanonical dynamics (and assuming ergodicity to the microcanonical ensemble). Note that a different explanation was advocated in Ref. 200 (see also Ref. 201, in particular Section VIII.B and C), which was however revised in Ref. 40. A discussion similar in spirit to the one outlined here[197] is provided in Ref. 222, see in particular Section 3.2 and 3.3.

Given the adiabatic separation and the stability of the propagation, the central question remains if the forces acting on the nuclei are actually the "correct" ones in Car–Parrinello molecular dynamics. As a reference serve the forces obtained from full self–consistent minimizations of the electronic energy $\min_{\{\psi_i\}}\langle\Psi_0|\mathcal{H}_{\mathrm{e}}|\Psi_0\rangle$ at each time step, i.e. Born–Oppenheimer molecular dynamics with extremely well converged wave functions. This is indeed the case as demonstrated in Figure 4(a): the physically meaningful dynamics of the x–component of the force acting on one silicon atom in the model system obtained from stable Car–Parrinello fictitious dynamics propagation of the electrons and from iterative minimizations of the electronic energy are extremely close.

Better resolution of one oscillation period in (b) reveals that the gross deviations are also oscillatory but that they are four orders of magnitudes smaller than the physical variations of the force resolved in Figure 4(a). These correspond to the "large–amplitude" oscillations of T_{e} visible in Figure 3 due to the drag of the nuclei exerted on the quasi–adiabatically following electrons having a *finite* dynamical mass μ. Note that the inertia of the electrons also dampens artificially the nuclear motion (typically on a few–percent scale, see Section V.C.2 in Ref. 28 for an analysis and a renormalization correction of M_I) but decreases as the fictitious mass approaches the adiabatic limit $\mu \to 0$. Superimposed on the gross variation in (b) are again high–frequency *bound oscillatory small–amplitude* fluctuations like for T_{e}. They lead *on physically relevant time scales* (i.e. those visible in Figure 4(a)) to "averaged forces" that are very close to the exact ground–state Born–Oppenheimer forces. This feature is an important ingredient in the derivation of adiabatic dynamics[197,177].

In conclusion, the Car–Parrinello force can be said to deviate at most instants of time from the exact Born–Oppenheimer force. However, this does not disturb the physical time

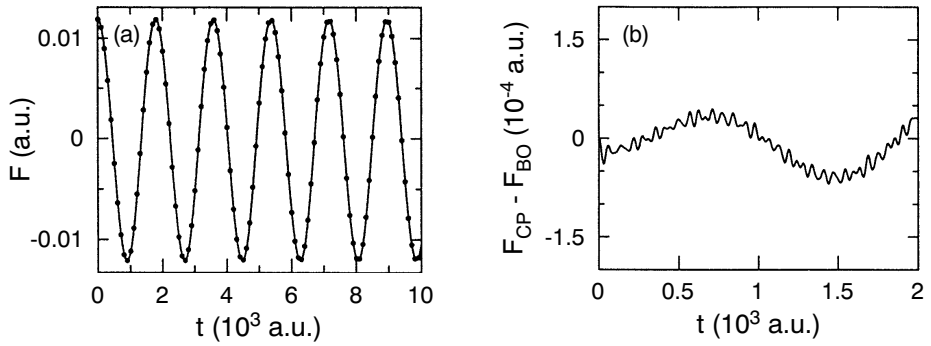

Figure 4. (a) Comparison of the x–component of the force acting on one atom of a model system obtained from Car–Parrinello (solid line) and well–converged Born–Oppenheimer (dots) molecular dynamics. (b) Enlarged view of the difference between Car–Parrinello and Born–Oppenheimer forces; for further details see text. Adapted from Ref. 197.

evolution due to (i) the smallness and boundedness of this difference *and* (ii) the intrinsic averaging effect of small–amplitude high–frequency oscillations within a few molecular dynamics time steps, i.e. on the sub–femtosecond time scale which is irrelevant for *nuclear* dynamics.

2.4.4 How to Control Adiabaticity ?

An important question is under which circumstances the adiabatic separation can be achieved, and how it can be controlled. A simple harmonic analysis of the frequency spectrum of the orbital classical fields close to the minimum defining the ground state yields[197]

$$\omega_{ij} = \left(\frac{2(\epsilon_i - \epsilon_j)}{\mu} \right)^{1/2} \quad , \tag{52}$$

where ϵ_j and ϵ_i are the eigenvalues of occupied and unoccupied orbitals, respectively; see Eq. (26) in Ref. 197 for the case where both orbitals are occupied ones. It can be seen from Figure 2 that the harmonic approximation works faithfully as compared to the exact spectrum; see Ref. 199 and Section IV.A in Ref. 201 for a more general analysis of the associated equations of motion. Since this is in particular true for the lowest frequency $\omega_{\rm e}^{\rm min}$, the handy analytic estimate for the lowest possible electronic frequency

$$\omega_{\rm e}^{\rm min} \propto \left(\frac{E_{\rm gap}}{\mu} \right)^{1/2} \quad , \tag{53}$$

shows that this frequency increases like the square root of the electronic energy difference $E_{\rm gap}$ between the lowest unoccupied and the highest occupied orbital. On the other hand it increases similarly for a decreasing fictitious mass parameter μ.

In order to guarantee the adiabatic separation, the frequency difference $\omega_{\rm e}^{\rm min} - \omega_{\rm n}^{\rm max}$ should be large, see Section 3.3 in Ref. 222 for a similar argument. But both the highest phonon frequency $\omega_{\rm n}^{\rm max}$ and the energy gap $E_{\rm gap}$ are quantities that a dictated by the

physics of the system. Whence, the only parameter in our hands to control adiabatic separation is the fictitious mass, which is therefore also called "adiabaticity parameter". However, decreasing μ not only shifts the electronic spectrum upwards on the frequency scale, but also stretches the entire frequency spectrum according to Eq. (52). This leads to an increase of the maximum frequency according to

$$\omega_{\mathrm{e}}^{\max} \propto \left(\frac{E_{\mathrm{cut}}}{\mu}\right)^{1/2} \quad , \tag{54}$$

where E_{cut} is the largest kinetic energy in an expansion of the wave function in terms of a plane wave basis set.

At this place a limitation to decrease μ arbitrarily kicks in due to the maximum length of the molecular dynamics time step $\Delta t^{\max}$ that can be used. The time step is inversely proportional to the highest frequency in the system, which is $\omega_{\mathrm{e}}^{\max}$ and thus the relation

$$\Delta t^{\max} \propto \left(\frac{\mu}{E_{\mathrm{cut}}}\right)^{1/2} \tag{55}$$

governs the largest time step that is possible. As a consequence, Car–Parrinello simulators have to find their way between Scylla and Charybdis and have to make a compromise on the control parameter μ; typical values for large–gap systems are μ = 500–1500 a.u. together with a time step of about 5–10 a.u. (0.12–0.24 fs). Recently, an algorithm was devised that optimizes μ during a particular simulation given a fixed accuracy criterion[34]. Note that a poor man's way to keep the time step large and still increase μ in order to satisfy adiabaticity is to choose heavier nuclear masses. That depresses the largest phonon or vibrational frequency $\omega_{\mathrm{n}}^{\max}$ of the nuclei (at the cost of renormalizing all *dynamical* quantities in the sense of classical isotope effects).

Up to this point the entire discussion of the stability and adiabaticity issues was based on model systems, approximate and mostly qualitative in nature. But recently it was actually proven[33] that the deviation or the absolute error Δ_μ of the Car–Parrinello trajectory relative to the trajectory obtained on the exact Born–Oppenheimer potential energy surface is controlled by μ:
Theorem 1 iv.): There are constants $C > 0$ and $\mu^\star > 0$ such that

$$\Delta_\mu = \left|\mathbf{R}^\mu(t) - \mathbf{R}^0(t)\right| + \left|\,|\psi^\mu;t\rangle - \left|\psi^0;t\right\rangle\right| \leq C\mu^{1/2} \quad , \; 0 \leq t \leq T \tag{56}$$

and the fictitious kinetic energy satisfies

$$T_{\mathrm{e}} = \mu\left\langle\dot{\psi}^\mu;t\middle|\dot{\psi}^\mu;t\right\rangle \leq C\mu \quad , \; 0 \leq t \leq T \tag{57}$$

for all values of the parameter μ satisfying $0 < \mu \leq \mu^\star$, where up to time $T > 0$ there exists a unique nuclear trajectory on the exact Born–Oppenheimer surface with $\omega_{\mathrm{e}}^{\min} > 0$ for $0 \leq t \leq T$, i.e. there is "always" a finite electronic excitation gap. Here, the superscript μ or 0 indicates that the trajectory was obtained via Car–Parrinello molecular dynamics using a finite mass μ or via dynamics on the exact Born–Oppenheimer surface, respectively. Note that not only the nuclear trajectory is shown to be close to the correct one, but also the wave function is proven to stay close to the fully converged one up to time T. Furthermore, it was also investigated what happens if the initial wave function at $t = 0$ is not the minimum of the electronic energy $\langle\mathcal{H}_{\mathrm{e}}\rangle$ but trapped in an excited state. In this case it is found that the propagated wave function will keep on oscillating at $t > 0$

also for $\mu \to 0$ and not even time averages converge to any of the eigenstates. Note that this does not preclude Car–Parrinello molecular dynamics in excited states, which is possible given a properly "minimizable" expression for the electronic energy, see e.g. Refs. 125, 86. However, this finding might have crucial implications for electronic level–crossing situations[65].

What happens if the electronic gap is very small or even vanishes $E_{\rm gap} \to 0$ as is the case for metallic systems? In this limit, all the above–given arguments break down due to the occurrence of zero–frequency electronic modes in the power spectrum according to Eq. (53), which necessarily overlap with the phonon spectrum. Following an idea of Sprik[242] applied in a classical context it was shown that the coupling of separate Nosé–Hoover thermostats[4, 118, 88] to the nuclear and electronic subsystem can maintain adiabaticity by counterbalancing the energy flow from ions to electrons so that the electrons stay "cool"[27]; see Ref. 84 for a similar idea to restore adiabaticity and Refs. 263,187,29 for analyses and improvements. Although this method is demonstrated to work in practice[196], this *ad hoc* cure is not entirely satisfactory from both a theoretical and practical point of view so that the well–controlled Born–Oppenheimer approach is recommended for strongly metallic systems. An additional advantage for metallic systems is that the latter is also better suited to sample many $\mathbf{k}$–points allows easily for fractional occupation numbers[194, 66, 176], and can handle efficiently the so–called charge sloshing problem[201].

2.4.5 The Quantum Chemistry Viewpoint

In order to understand Car–Parrinello molecular dynamics also from the "quantum chemistry perspective", it is useful to formulate it for the special case of the Hartree–Fock approximation using

$$\begin{aligned}\mathcal{L}_{\rm CP} = & \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \mu \left\langle \dot{\psi}_i \middle| \dot{\psi}_i \right\rangle \\ & - \left\langle \Psi_0 | \mathcal{H}_{\rm e}^{\rm HF} | \Psi_0 \right\rangle + \sum_{i,j} \Lambda_{ij} \left(\langle \psi_i | \psi_j \rangle - \delta_{ij} \right) \quad . \end{aligned} \tag{58}$$

The resulting equations of motion

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \left\langle \Psi_0 \middle| \mathcal{H}_{\rm e}^{\rm HF} \middle| \Psi_0 \right\rangle \tag{59}$$

$$\mu \ddot{\psi}_i(t) = -\mathcal{H}_{\rm e}^{\rm HF} \psi_i + \sum_j \Lambda_{ij} \psi_j \tag{60}$$

are very close to those obtained for Born–Oppenheimer molecular dynamics Eqs. (39)–(40) except for (i) no need to minimize the electronic total energy expression and (ii) featuring the additional fictitious kinetic energy term associated to the orbital degrees of freedom. It is suggestive to argue that both sets of equations become identical if the term $|\mu \ddot{\psi}_i(t)|$ is small at any time t compared to the physically relevant forces on the right–hand–side of both Eq. (59) and Eq. (60). This term being zero (or small) means that one is at (or close to) the minimum of the electronic energy $\langle \Psi_0 | \mathcal{H}_{\rm e}^{\rm HF} | \Psi_0 \rangle$ since time derivatives of the orbitals $\{\psi_i\}$ can be considered as variations of Ψ_0 and thus of the expectation value $\langle \mathcal{H}_{\rm e}^{\rm HF} \rangle$ itself. In other words, no forces act on the wave function if $\mu \ddot{\psi}_i \equiv 0$. In conclusion, the Car–Parrinello equations are expected to produce the correct dynamics and thus physical

trajectories in the microcanonical ensemble in this idealized limit. But if $|\mu\ddot{\psi}_i(t)|$ is small for all i, this also implies that the associated kinetic energy $T_\mathrm{e} = \sum_i \mu\langle\dot{\psi}_i|\dot{\psi}_i\rangle$ is small, which connects these more qualitative arguments with the previous discussion[197].

At this stage, it is also interesting to compare the structure of the Lagrangian Eq. (58) and the Euler–Lagrange equation Eq. (43) for Car–Parrinello dynamics to the analogues Eqs. (36) and (37), respectively, used to derive "Hartree–Fock statics". The former reduce to the latter if the dynamical aspect and the associated time evolution is neglected, that is in the limit that the nuclear and electronic momenta are absent or constant. Thus, the Car–Parrinello ansatz, namely Eq. (41) together with Eqs. (42)–(43), can also be viewed as a prescription to derive a new class of "dynamical *ab initio* methods" in very general terms.

2.4.6 The Simulated Annealing and Optimization Viewpoints

In the discussion given above, Car–Parrinello molecular dynamics was motivated by "combining" the positive features of both Ehrenfest and Born–Oppenheimer molecular dynamics as much as possible. Looked at from another side, the Car–Parrinello method can also be considered as an ingenious way to perform *global* optimizations (minimizations) of nonlinear functions, here $\langle\Psi_0|\mathcal{H}_\mathrm{e}|\Psi_0\rangle$, in a high–dimensional parameter space including complicated constraints. The optimization parameters are those used to represent the total wave function Ψ_0 in terms of simpler functions, for instance expansion coefficients of the orbitals in terms of Gaussians or plane waves, see e.g. Refs. 242, 173, 288, 253 for applications of the same idea in other fields.

Keeping the nuclei frozen for a moment, one could start this optimization procedure from a "random wave function" which certainly does not minimize the electronic energy. Thus, its fictitious kinetic energy is high, the electronic degrees of freedom are "hot". This energy, however, can be extracted from the system by systematically cooling it to lower and lower temperatures. This can be achieved in an elegant way by adding a non–conservative damping term to the electronic Car–Parrinello equation of motion Eq. (45)

$$\mu\ddot{\psi}_i(t) = -\frac{\delta}{\delta\psi_i^\star}\langle\Psi_0|\mathcal{H}_\mathrm{e}|\Psi_0\rangle + \frac{\delta}{\delta\psi_i^\star}\{\textit{constraints}\} - \gamma_\mathrm{e}\mu\dot{\psi}_i \quad , \tag{61}$$

where $\gamma_\mathrm{e} \geq 0$ is a friction constant that governs the rate of energy dissipation[256]; alternatively, dissipation can be enforced in a discrete fashion by reducing the velocities by multiplying them with a constant factor < 1. Note that this deterministic and dynamical method is very similar in spirit to simulated annealing[152] invented in the framework of the stochastic Monte Carlo approach in the canonical ensemble. If the energy dissipation is done slowly, the wave function will find its way down to the minimum of the energy. At the end, an intricate global optimization has been performed!

If the nuclei are allowed to move according to Eq. (44) in the presence of another damping term a combined or simultaneous optimization of both electrons and nuclei can be achieved, which amounts to a "global geometry optimization". This perspective is stressed in more detail in the review Ref. 91 and an implementation of such ideas within the CADPAC quantum chemistry code is described in Ref. 287. This operational mode of Car–Parrinello molecular dynamics is related to other optimization techniques where it is aimed to optimize simultaneously both the structure of the nuclear skeleton and the electronic structure. This is achieved by considering the nuclear coordinates and the expansion

coefficients of the orbitals as variation parameters on the same footing[21,130,253]. But Car–Parrinello molecular dynamics is more than that because even if the nuclei continuously move according to Newtonian dynamics at finite temperature an initially optimized wave function will stay optimal along the nuclear trajectory.

2.4.7 The Extended Lagrangian Viewpoint

There is still another way to look at the Car–Parrinello method, namely in the light of so–called "extended Lagrangians" or "extended system dynamics"[5], see e.g. Refs. 48, 4, 118, 244, 88 for introductions. The basic idea is to couple additional degrees of freedom to the Lagrangian of interest, thereby "extending" it by increasing the dimensionality of phase space. These degrees of freedom are treated like classical particle coordinates, i.e. they are in general characterized by "positions", "momenta", "masses", "interactions" and a "coupling term" to the particle's positions and momenta. In order to distinguish them from the physical degrees of freedom, they are often called "fictitious degrees of freedom".

The corresponding equations of motion follow from the Euler–Lagrange equations and yield a microcanonical ensemble in the extended phase space where the Hamiltonian of the extended system is strictly conserved. In other words, the Hamiltonian of the physical (sub–) system is no more (strictly) conserved, and the produced ensemble is no more the microcanonical one. Any extended system dynamics is constructed such that time–averages taken in that part of phase space that is associated to the physical degrees of freedom (obtained from a partial trace over the fictitious degrees of freedom) are physically meaningful. Of course, dynamics and thermodynamics of the system are affected by adding fictitious degrees of freedom, the classic examples being temperature and pressure control by thermostats and barostats.

In the case of Car–Parrinello molecular dynamics, the basic Lagrangian for Newtonian dynamics of the nuclei is actually extended by classical *fields* $\{\psi_i(\mathbf{r})\}$, i.e. functions instead of coordinates, which represent the quantum wave function. Thus, vector products or absolute values have to be generalized to scalar products and norms of the fields. In addition, the "positions" of these fields $\{\psi_i\}$ actually have a physical meaning, contrary to their momenta $\{\dot{\psi}_i\}$.

2.5 What about Hellmann–Feynman Forces ?

An important ingredient in all dynamics methods is the efficient calculation of the forces acting on the nuclei, see Eqs. (30), (32), and (44). The straightforward numerical evaluation of the derivative

$$\mathbf{F}_I = -\nabla_I \langle \Psi_0 | \mathcal{H}_\mathrm{e} | \Psi_0 \rangle \tag{62}$$

in terms of a finite–difference approximation of the total electronic energy is both too costly and too inaccurate for dynamical simulations. What happens if the gradients are evaluated analytically? In addition to the derivative of the Hamiltonian itself

$$\begin{aligned} \nabla_I \langle \Psi_0 | \mathcal{H}_\mathrm{e} | \Psi_0 \rangle = & \langle \Psi_0 | \nabla_I \mathcal{H}_\mathrm{e} | \Psi_0 \rangle \\ & + \langle \nabla_I \Psi_0 | \mathcal{H}_\mathrm{e} | \Psi_0 \rangle + \langle \Psi_0 | \mathcal{H}_\mathrm{e} | \nabla_I \Psi_0 \rangle \end{aligned} \tag{63}$$

there are in general also contributions from variations of the wave function $\sim \nabla_I \Psi_0$. In general means here that these contributions vanish exactly

$$\mathbf{F}_I^{\mathrm{HFT}} = -\langle \Psi_0 | \nabla_I \mathcal{H}_{\mathrm{e}} | \Psi_0 \rangle \tag{64}$$

if the wave function is an exact eigenfunction (or stationary state wave function) of the particular Hamiltonian under consideration. This is the content of the often–cited Hellmann–Feynman Theorem[133,76,168], which is also valid for many variational wave functions (e.g. the Hartree–Fock wave function) provided that *complete basis sets* are used. If this is not the case, which has to be assumed for numerical calculations, the additional terms have to be evaluated explicitly.

In order to proceed a Slater determinant $\Psi_0 = \det\{\psi_i\}$ of one–particle orbitals ψ_i, which themselves are expanded

$$\psi_i = \sum_\nu c_{i\nu}\ f_\nu(\mathbf{r}; \{\mathbf{R}_I\}) \tag{65}$$

in terms of a linear combination of basis functions $\{f_\nu\}$, is used in conjunction with an effective one–particle Hamiltonian (such as e.g. in Hartree–Fock or Kohn–Sham theories). The basis functions might depend explicitly on the nuclear positions (in the case of basis functions with origin such as atom–centered orbitals), whereas the expansion coefficients always carry an implicit dependence. This means that from the outset two sorts of forces are expected

$$\nabla_I \psi_i = \sum_\nu (\nabla_I c_{i\nu})\ f_\nu(\mathbf{r}; \{\mathbf{R}_I\}) + \sum_\nu c_{i\nu}\ (\nabla_I f_\nu(\mathbf{r}; \{\mathbf{R}_I\})) \tag{66}$$

in addition to the Hellmann–Feynman force Eq. (64).

Using such a linear expansion Eq. (65), the force contributions stemming from the nuclear gradients of the wave function in Eq. (63) can be disentangled into two terms. The first one is called "incomplete–basis–set correction" (IBS) in solid state theory[21,247,73] and corresponds to the "wave function force"[215] or "Pulay force" in quantum chemistry[215,216]. It contains the nuclear gradients of the basis functions

$$\mathbf{F}_I^{\mathrm{IBS}} = -\sum_{i\nu\mu} \left(\left\langle \nabla_I f_\nu \left| \mathcal{H}_{\mathrm{e}}^{\mathrm{NSC}} - \epsilon_i \right| f_\mu \right\rangle + \left\langle f_\nu \left| \mathcal{H}_{\mathrm{e}}^{\mathrm{NSC}} - \epsilon_i \right| \nabla f_\mu \right\rangle \right) \tag{67}$$

and the (in practice non–self–consistent) effective one–particle Hamiltonian[21,247]. The second term leads to the so–called "non–self–consistency correction" (NSC) of the force[21,247]

$$\mathbf{F}_I^{\mathrm{NSC}} = -\int d\mathbf{r}\ (\nabla_I n) \left(V^{\mathrm{SCF}} - V^{\mathrm{NSC}} \right) \tag{68}$$

and is governed by the difference between the self–consistent ("exact") potential or field V^{SCF} and its non–self–consistent (or approximate) counterpart V^{NSC} associated to $\mathcal{H}_{\mathrm{e}}^{\mathrm{NSC}}$; $n(\mathbf{r})$ is the charge density. In summary, the total force needed in *ab initio* molecular dynamics simulations

$$\mathbf{F}_I = \mathbf{F}_I^{\mathrm{HFT}} + \mathbf{F}_I^{\mathrm{IBS}} + \mathbf{F}_I^{\mathrm{NSC}} \tag{69}$$

comprises in general three qualitatively different terms; see the tutorial article Ref. 73 for a further discussion of core vs. valence states and the effect of pseudopotentials. Assuming that self–consistency is exactly satisfied (which is *never* going to be the case in numerical

calculations), the force $\mathbf{F}_I^{\mathrm{NSC}}$ vanishes and $\mathcal{H}_{\mathrm{e}}^{\mathrm{SCF}}$ has to be used to evaluate $\mathbf{F}_I^{\mathrm{IBS}}$. The Pulay contribution vanishes in the limit of using a complete basis set (which is also not possible to achieve in actual calculations).

The most obvious simplification arises if the wave function is expanded in terms of originless basis functions such as plane waves, see Eq. (100). In this case the Pulay force vanishes exactly, which applies of course to all *ab initio* molecular dynamics schemes (i.e. Ehrenfest, Born–Oppenheimer, and Car–Parrinello) using that particular basis set. This statement is true for calculations where the number of plane waves is fixed. If the number of plane waves changes, such as in (constant pressure) calculations with varying cell volume / shape where the energy cutoff is strictly fixed instead, Pulay stress contributions crop up[89, 105, 275, 85, 82]. If basis sets with origin are used instead of plane waves Pulay forces arise always and have to be included explicitly in force calculations, see e.g. Refs. 28, 170, 171 for such methods. Another interesting simplification of the same origin is noted in passing: there is no basis set superposition error (BSSE)[35] in plane wave–based electronic structure calculations.

A non–obvious and more delicate term in the context of *ab initio* molecular dynamics is the one stemming from non–self–consistency Eq. (68). This term vanishes only if the wave function Ψ_0 is an eigenfunction of the Hamiltonian *within the subspace spanned by the finite basis set used*. This demands less than the Hellmann–Feynman theorem where Ψ_0 has to be an exact eigenfunction of the Hamiltonian and a complete basis set has to be used in turn. In terms of electronic structure calculations complete self–consistency (within a given incomplete basis set) has to be reached in order that $\mathbf{F}_I^{\mathrm{NSC}}$ vanishes. Thus, in numerical calculations the NSC term can be made arbitrarily small by optimizing the effective Hamiltonian and by determining its eigenfunctions to very high accuracy, but it can never be suppressed completely.

The crucial point is, however, that in Car–Parrinello as well as in Ehrenfest molecular dynamics it is not the minimized expectation value of the electronic Hamiltonian, i.e. $\min_{\Psi_0}\{\langle\Psi_0|\mathcal{H}_{\mathrm{e}}|\Psi_0\rangle\}$, that yields the consistent forces. What is merely needed is to evaluate the expression $\langle\Psi_0|\mathcal{H}_{\mathrm{e}}|\Psi_0\rangle$ with the Hamiltonian and the associated wave function available at a certain time step, compare Eq. (32) to Eq. (44) or Eq. (30). In other words, it is not required (concerning the present discussion of the contributions to the force!) that the expectation value of the electronic Hamiltonian is actually completely minimized for the nuclear configuration at that time step. Whence, full self–consistency is not required for this purpose in the case of Car–Parrinello (and Ehrenfest) molecular dynamics. As a consequence, the non–self–consistency correction to the force $\mathbf{F}_I^{\mathrm{NSC}}$ Eq. (68) is irrelevant in Car–Parrinello (and Ehrenfest) simulations.

In Born–Oppenheimer molecular dynamics, on the other hand, the expectation value of the Hamiltonian has to be minimized for each nuclear configuration before taking the gradient to obtain the consistent force! In this scheme there is (independently from the issue of Pulay forces) *always* the non–vanishing contribution of the non–self–consistency force, which is unknown by its very definition (if it were know, the problem was solved, see Eq. (68)). It is noted in passing that there are estimation schemes available that correct *approximately* for this systematic error in Born–Oppenheimer dynamics and lead to significant time–savings, see e.g. Ref. 159.

Heuristically one could also argue that within Car–Parrinello dynamics the non–vanishing non–self–consistency force is kept under control or counterbalanced by the non–

vanishing "mass times acceleration term" $\mu\ddot{\psi}_i(t) \approx 0$, which is small but not identical to zero and oscillatory. This is sufficient to keep the propagation stable, whereas $\mu\ddot{\psi}_i(t) \equiv 0$, i.e. an extremely tight minimization $\min_{\Psi_0}\{\langle\Psi_0|\mathcal{H}_{\rm e}|\Psi_0\rangle\}$, is required by its very definition in order to make the Born–Oppenheimer approach stable, compare again Eq. (60) to Eq. (40). Thus, also from this perspective it becomes clear that the fictitious kinetic energy of the electrons and thus their fictitious temperature is a measure for the departure from the exact Born–Oppenheimer surface during Car–Parrinello dynamics.

Finally, the present discussion shows that nowhere in these force derivations was *made use of* the Hellmann–Feynman theorem as is sometimes stated. Actually, it is known for a long time that this theorem is quite useless for numerical electronic structure calculations, see e.g. Refs. 215, 21, 216 and references therein. Rather *it turns out* that in the case of Car–Parrinello calculations using a plane wave basis the resulting relation for the force, namely Eq. (64), looks like the one obtained by simply invoking the Hellmann–Feynman theorem at the outset.

It is interesting to recall that the Hellmann–Feynman theorem as applied to a non–eigenfunction of a Hamiltonian yields only a first–order perturbative estimate of the exact force[133,168]. The same argument applies to *ab initio* molecular dynamics calculations where possible force corrections according to Eqs. (67) and (68) are neglected without justification. Furthermore, such simulations can of course not strictly conserve the total Hamiltonian $E_{\rm cons}$ Eq. (48). Finally, it should be stressed that possible contributions to the force in the nuclear equation of motion Eq. (44) due to *position–dependent* wave function *constraints* have to be evaluated following the same procedure. This leads to similar "correction terms" to the force, see e.g. Ref. 163 for such a case.

2.6 Which Method to Choose ?

Presumably the most important question for practical applications is which *ab initio* molecular dynamics method is the most efficient in terms of computer time given a specific problem. An *a priori* advantage of both the Ehrenfest and Car–Parrinello schemes over Born–Oppenheimer molecular dynamics is that no diagonalization of the Hamiltonian (or the equivalent minimization of an energy functional) is necessary, except at the very first step in order to obtain the initial wave function. The difference is, however, that the Ehrenfest time–evolution according to the time–dependent Schrödinger equation Eq. (26) conforms to a unitary propagation[156,167,157]

$$\Psi(t_0+\Delta t) = \exp\left[-i\mathcal{H}_{\rm e}(t_0)\Delta t/\hbar\right]\Psi(t_0) \tag{70}$$

$$\begin{aligned}\Psi(t_0+m\,\Delta t) = {} & \exp\left[-i\mathcal{H}_{\rm e}(t_0+(m-1)\Delta t)\;\Delta t/\hbar\right] \\ & \times\cdots \\ & \times\exp\left[-i\mathcal{H}_{\rm e}(t_0+2\Delta t)\;\Delta t/\hbar\right] \\ & \times\exp\left[-i\mathcal{H}_{\rm e}(t_0+\Delta t)\;\Delta t/\hbar\right] \\ & \times\exp\left[-i\mathcal{H}_{\rm e}(t_0)\;\Delta t/\hbar\right]\Psi(t_0)\end{aligned} \tag{71}$$

$$\Psi(t_0+t^{\rm max}) \stackrel{\Delta t\to 0}{=} \mathsf{T}\exp\left[-\frac{i}{\hbar}\int_{t_0}^{t_0+t^{\rm max}} dt\,\mathcal{H}_{\rm e}(t)\right]\Psi(t_0) \tag{72}$$

for infinitesimally short times given by the time step $\Delta t = t^{\rm max}/m$; here T is the time–ordering operator and $\mathcal{H}_{\rm e}(t)$ is the Hamiltonian (which is *implicitly* time–dependent via

the positions $\{\mathbf{R}_I(t)\}$) evaluated at time t using e.g. split operator techniques[74]. Thus, the wave function Ψ will conserve its norm and in particular orbitals used to expand it will stay orthonormal, see e.g. Ref. 258. In Car–Parrinello molecular dynamics, on the contrary, the orthonormality has to be imposed brute force by Lagrange multipliers, which amounts to an additional orthogonalization at each molecular dynamics step. If this is not properly done, the orbitals will become non–orthogonal and the wave function unnormalized, see e.g. Section III.C.1 in Ref. 201.

But this theoretical disadvantage of Car–Parrinello vs. Ehrenfest dynamics is in reality more than compensated by the possibility to use a much larger time step in order to propagate the electronic (and thus nuclear) degrees of freedom in the former scheme. In both approaches, there is the time scale inherent to the nuclear motion τ_{n} and the one stemming from the electronic dynamics τ_{e}. The first one can be estimated by considering the highest phonon or vibrational frequency and amounts to the order of $\tau_{\mathrm{n}} \sim 10^{-14}$ s (or 0.01 ps or 10 fs, assuming a maximum frequency of about 4000 cm^{-1}). This time scale depends only on the physics of the problem under consideration and yields an upper limit for the time step $\Delta t^{\max}$ that can be used in order to integrate the equations of motion, e.g. $\Delta t^{\max} \approx \tau_{\mathrm{n}}/10$.

The fasted electronic motion in Ehrenfest dynamics can be estimated within a plane wave expansion by $\omega_{\mathrm{e}}^{\mathrm{E}} \sim E_{\mathrm{cut}}$, where E_{cut} is the maximum kinetic energy included in the expansion. A realistic estimate for reasonable basis sets is $\tau_{\mathrm{e}}^{\mathrm{E}} \sim 10^{-16}$ s, which leads to $\tau_{\mathrm{e}}^{\mathrm{E}} \approx \tau_{\mathrm{n}}/100$. The analogues relation for Car–Parrinello dynamics reads however $\omega_{\mathrm{e}}^{\mathrm{CP}} \sim (E_{\mathrm{cut}}/\mu)^{1/2}$ according to the analysis in Section 2.4, see Eq. (54). Thus, in addition to reducing $\omega_{\mathrm{e}}^{\mathrm{CP}}$ by introducing a finite electron mass μ, the maximum electronic frequency increases much more slowly in Car–Parrinello than in Ehrenfest molecular dynamics with increasing basis set size. An estimate for the same basis set and a typical fictitious mass yields about $\tau_{\mathrm{e}}^{\mathrm{CP}} \sim 10^{-15}$ s or $\tau_{\mathrm{e}}^{\mathrm{CP}} \approx \tau_{\mathrm{n}}/10$. According to this simple estimate, the time step can be about one order of magnitude larger if Car–Parrinello second–order fictitious–time electron dynamics is used instead of Ehrenfest first–order real–time electron dynamics.

The time scale and thus time step problem inherent to Ehrenfest dynamics prompted some attempts to cure it. In Ref. 83 the equations of motion of electrons and nuclei were integrated using two different time steps, the one of the nuclei being 20–times as large as the electronic one. The powerful technology of multiple–time step integration theory[262,264] could also be applied in order to ameliorate the time scale disparity[244]. A different approach borrowed from plasma simulations consists in decreasing the nuclear masses so that their time evolution is artificially speeded up[258]. As a result, the *nuclear* dynamics is fictitious (in the presence of real–time electron dynamics!) and has to be rescaled to the proper mass ratio after the simulation.

In both Ehrenfest and Car–Parrinello schemes the explicitly treated electron dynamics limits the largest time step that can be used in order to integrate simultaneously the coupled equations of motion for nuclei and electrons. This limitation does of course not exist in Born–Oppenheimer dynamics since there is no explicit electron dynamics so that the maximum time step is simply given by the one intrinsic to nuclear motion, i.e. $\tau_{\mathrm{e}}^{\mathrm{BO}} \approx \tau_{\mathrm{n}}$. This is formally an order of magnitude advantage with respect to Car–Parrinello dynamics.

Do these back–of–the–envelope estimates have anything to do with reality? Fortunately, several state–of–the–art studies are reported in the literature for physically similar

systems where all three molecular dynamics schemes have been employed. Ehrenfest simulations[233,83] of a dilute $K_x{\cdot}(KCl)_{1-x}$ melt were performed using a time step of 0.012–0.024 fs. In comparison, a time step as large as 0.4 fs could be used to produce a stable Car–Parrinello simulation of electrons in liquid ammonia[57,58]. Since the physics of these systems has a similar nature — "unbound electrons" dissolved in liquid condensed matter (localizing as F–centers, polarons, bipolarons, etc.) — the time step difference of about a factor of ten confirms the crude estimate given above. In a Born–Oppenheimer simulation[237] of again $K_x{\cdot}(KCl)_{1-x}$ but up to a higher concentration of unbound electrons the time step used was 0.5 fs.

The time–scale advantage of Born–Oppenheimer vs. Car–Parrinello dynamics becomes more evident if the nuclear dynamics becomes fairly slow, such as in liquid sodium[158] or selenium[151] where a time step of 3 fs was used. This establishes the above–mentioned order of magnitude advantage of Born–Oppenheimer vs. Car–Parrinello dynamics in advantageous cases. However, it has to be taken into account that in simulations[151] with such a large time step dynamical information is limited to about 10 THz, which corresponds to frequencies below roughly 500 cm^{-1}. In order to resolve vibrations in molecular systems with stiff covalent bonds the time step has to be decreased to less than a femtosecond (see the estimate given above) also in Born–Oppenheimer dynamics.

The comparison of the overall performance of Car–Parrinello and Born–Oppenheimer molecular dynamics in terms of computer time is a delicate issue. For instance it depends crucially on the choice made concerning the accuracy of the conservation of the energy $E_{\rm cons}$ as defined in Eq. (48). Thus, this issue is to some extend subject of "personal taste" as to what is considered to be a "sufficiently accurate" energy conservation. In addition, this comparison might to different conclusions as a function of system size. In order to nevertheless shed light on this point, microcanonical simulations of 8 silicon atoms were performed with various parameters using Car–Parrinello and Born–Oppenheimer molecular dynamics as implemented in the CPMD package[139]. This large–gap system was initially extremely well equilibrated and the runs were extended to 8 ps (and a few to 12 ps with no noticeable difference) at a temperature of about 360–370 K (with ± 80 K root–mean–square fluctuations). The wave function was expanded up to $E_{\rm cut} = 10$ Ry at the Γ–point of a simple cubic supercell and LDA was used to describe the interactions. In both cases the velocity Verlet scheme was used to integrate the equations of motion. It is noted in passing that also the velocity Verlet algorithm[263] allows for stable integration of the equations of motion contrary to the statements in Ref. 222 (see Section 3.4 and Figs. 4–5).

In Car–Parrinello molecular dynamics two different time steps were used, 5 a.u. and 10 a.u. (corresponding to about 0.24 fs), in conjunction with a fictitious electron mass of $\mu = 400$ a.u.; this mass parameter is certainly not optimized and thus the time step could be increased furthermore. Also the largest time step lead to perfect adiabaticity (similar to the one documented in Figure 3), i.e. $E_{\rm phys}$ Eq. (49) and $T_{\rm e}$ Eq. (51) did not show a systematic drift relative to the energy scale set by the variations of $V_{\rm e}$ Eq. (50). Within Born–Oppenheimer molecular dynamics the minimization of the energy functional was done using the highly efficient DIIS (direct inversion in the iterative subspace) scheme using 10 "history vectors". In this case, the time step was either 10 a.u. or 100 a.u. and three convergence criteria were used; note that the large time step corresponding to 2.4 fs is already at the limit to be used to investigate typical *molecular* systems (with frequencies up to 3–4000 cm^{-1}). The convergence criterion is based on the largest element of the wave

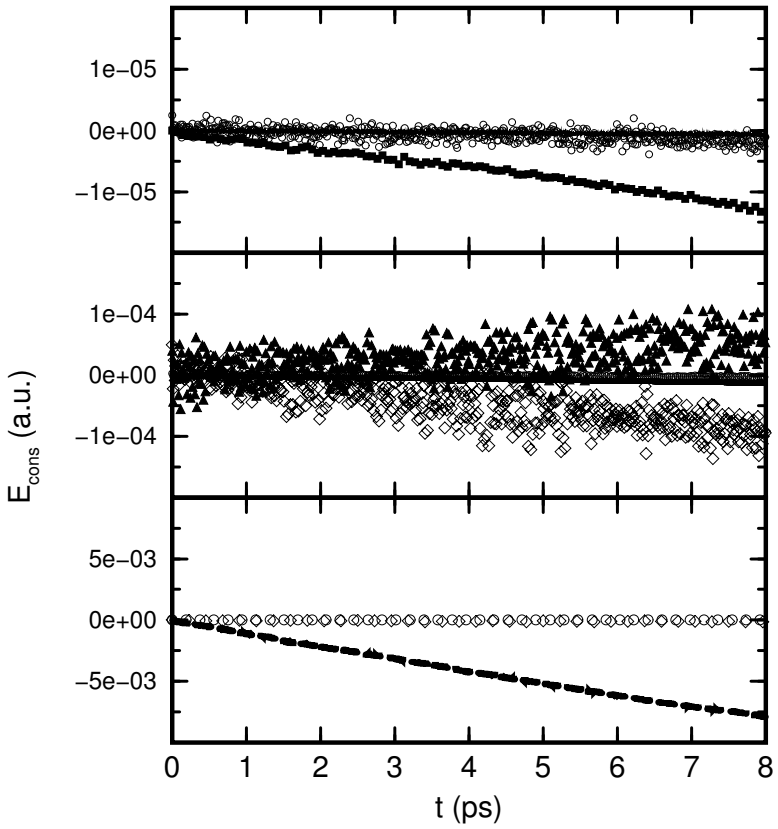

Figure 5. Conserved energy $E_{\rm cons}$ defined in Eq. (48) from Car–Parrinello (CP) and Born–Oppenheimer (BO) molecular dynamics simulations of a model system for various time steps and convergence criteria using the CPMD package[139]; see text for further details and Table 1 for the corresponding timings. Top: solid line: CP, 5 a.u.; open circles: CP, 10 a.u.; filled squares: BO, 10 a.u., 10^{-6}. Middle: open circles: CP, 10 a.u.; filled squares: BO, 10 a.u., 10^{-6}; filled triangles: BO, 100 a.u., 10^{-6}; open diamonds: BO, 100 a.u., 10^{-5}. Bottom: open circles: CP, 10 a.u.; open diamonds: BO, 100 a.u., 10^{-5}; dashed line: BO, 100 a.u., 10^{-4}.

function gradient which was required to be smaller than 10^{-6}, 10^{-5} or 10^{-4} a.u.; note that the resulting energy convergence shows roughly a quadratic dependence on this criterion.

The outcome of this comparison is shown in Figure 5 in terms of the time evolution of the conserved energy $E_{\rm cons}$ Eq. (48) on energy scales that cover more than three orders of magnitude in absolute accuracy. Within the present comparison ultimate energy stability was obtained using Car–Parrinello molecular dynamics with the shortest time step of 5 a.u., which conserves the energy of the total system to about 6×10^{-8} a.u. per picosecond, see solid line in Figure 5(top). Increasing the time step to 10 a.u. leads to an energy conservation of about 3×10^{-7} a.u./ps and much larger energy fluctuations, see open circles

Table 1. Timings in CPU seconds and energy conservation in a.u. / ps for Car–Parrinello (CP) and Born–Oppenheimer (BO) molecular dynamics simulations of a model system for 1 ps of trajectory on an IBM RS6000 / model 390 (Power2) workstation using the CPMD package[139]; see Figure 5 for corresponding energy plots.

Method	Time step (a.u.)	Convergence (a.u.)	Conservation (a.u./ps)	Time (s)
CP	5	—	6×10^{-8}	3230
CP	7	—	1×10^{-7}	2310
CP	10	—	3×10^{-7}	1610
BO	10	10^{-6}	1×10^{-6}	16590
BO	50	10^{-6}	1×10^{-6}	4130
BO	100	10^{-6}	6×10^{-6}	2250
BO	100	10^{-5}	1×10^{-5}	1660
BO	100	10^{-4}	1×10^{-3}	1060

in Figure 5(top). The computer time needed in order to generate one picosecond of Car–Parrinello trajectory increases – to a good approximation – linearly with the increasing time step, see Table 1. The most stable Born–Oppenheimer run was performed with a time step of 10 a.u. and a convergence of 10^{-6}. This leads to an energy conservation of about 1×10^{-6} a.u./ps, see filled squares in Figure 5(top).

As the maximum time step in Born–Oppenheimer dynamics is only related to the time scale associated to nuclear motion it could be increased from 10 to 100 a.u. while keeping the convergence at the same tight limit of 10^{-6}. This worsens the energy conservation slightly (to about 6×10^{-6} a.u./ps), whereas the energy *fluctuations* increase dramatically, see filled triangles in Figure 5(middle) and note the change of scale compared to Figure 5(top). The overall gain is an acceleration of the Born–Oppenheimer simulation by a factor of about seven to eight, see Table 1. In the Born–Oppenheimer scheme, the computer time needed for a fixed amount of simulated physical time decreases only sublinearly with increasing time step since the initial guess for the iterative minimization degrades in quality as the time step is made larger. Further savings of computer time can be easily achieved by decreasing the quality of the wave function convergence from 10^{-6} to 10^{-5} and finally to 10^{-4}, see Table 1. This is unfortunately tied to a significant decrease of the energy conservation from 6×10^{-6} a.u./ps at 10^{-6} (filled triangles) to about 1×10^{-3} a.u./ps at 10^{-4} (dashed line) using the same 100 a.u. time step, see Figure 5(bottom) but note the change of scale compared to Figure 5(middle).

In conclusion, Born–Oppenheimer molecular dynamics can be made as fast as (or even faster than) Car–Parrinello molecular dynamics (as measured by the amount of CPU time spent per picosecond) at the expense of sacrificing accuracy in terms of energy conservation. In the "classical molecular dynamics community" there is a general consensus that this conservation law should be taken seriously being a measure of the numerical quality of the simulation. In the "quantum chemistry and total energy communities" this issue is typically of less concern. There, it is rather the quality of the convergence of the wave function or energy (as achieved in every individual molecular dynamics step) that is believed to be crucial in order to gauge the quality of a particular simulation.

Finally, it is worth commenting in this particular section on a paper entitled "A comparison of Car–Parrinello and Born–Oppenheimer generalized valence bond molecular dynamics"[94]. In this paper one (computationally expensive) term in the nuclear equations of motion is neglected[269,178]. It is well known that using a basis set with origin, such as

Gaussians $f_\nu^{\mathrm{G}}(\mathbf{r};\{\mathbf{R}_I\})$ centered at the nuclei, see Eq. (99), produces various Pulay forces, see Section 2.5. In particular a linear expansion Eq. (65) or Eq. (97) based on such orbitals introduces a position dependence into the orthogonality constraint

$$\langle\psi_i|\psi_j\rangle = \sum_{\nu\mu} c_{i\nu}^\star c_{j\mu} \underbrace{\left\langle f_\nu^{\mathrm{G}} \,\middle|\, f_\mu^{\mathrm{G}} \right\rangle}_{S_{\nu\mu}} = \delta_{ij} \tag{73}$$

that is hidden in the overlap matrix $S_{\nu\mu}(\{\mathbf{R}_I\})$ which involves the basis functions. According to Eq. (44) this term produces a constraint force of the type

$$\sum_{ij} \Lambda_{ij} \sum_{\nu\mu} c_{i\nu}^\star c_{j\mu} \frac{\partial}{\partial \mathbf{R}_I} S_{\nu\mu}(\{\mathbf{R}_I\}) \tag{74}$$

in the correct Car–Parrinello equation of motion *for the nuclei* similar to the one contained in the electronic equation of motion Eq. (45). This term has to be included in order to yield exact Car–Parrinello trajectories and thus energy conservation, see e.g. Eq. (37) in Ref. 163 for a similar situation. In the case of Born–Oppenheimer molecular dynamics, on the contrary, this term is always absent in the nuclear equation of motion, see Eq. (32). Thus, the particular implementation[94] underlying the comparison between Car–Parrinello and Born–Oppenheimer molecular dynamics is an approximate one from the outset concerning the Car–Parrinello part; it can be argued that this was justified in the early papers[125,126] where the basic feasibility of both the Hartree-Fock– and generalized valence bond–based Car–Parrinello molecular dynamics techniques was demonstrated[129]. Most importantly, this approximation implies that the energy E_{cons} Eq. (48) *cannot be rigorously conserved* in this particular version of Car–Parrinello molecular dynamics. However, energy conservation of E_{cons} was used in Ref. 94 to compare the efficiency and accuracy of these two approaches to GVB *ab initio* molecular dynamics (using DIIS for the Born–Oppenheimer simulations as done in the above–given comparison). Thus, the final conclusion that for "... approaches that utilize non–space–fixed bases to describe the electronic wave function, Born–Oppenheimer AIMD is the method of choice, both in terms of accuracy and speed"[94] cannot be drawn from this specific comparison for the reasons outlined above (independently of the particular basis set or electronic structure method used).

The toy system investigated here (see Figure 5 and Table 1), i.e. 8 silicon atoms in a periodic supercell, is for the purpose of comparing different approaches to *ab initio* molecular dynamics quite similar to the system used in Ref. 94, i.e. clusters of 4 or 6 sodium atoms (in addition, qualitatively identical results where reported in Section 4 for silicon clusters). Thus, it is admissible to compare the energy conservations reported in Figs. 1 and 2 of Ref. 94 to the ones depicted here in Figure 5 noting that the longest simulations reported in Ref. 94 reached only 1 ps. It should be stressed that the energy conservation seen in Figure 5(top) is routinely achieved in Car–Parrinello molecular dynamics simulations.

2.7 Electronic Structure Methods

2.7.1 Introduction

Up to this point, the electronic structure method to calculate the *ab initio* forces $\nabla_I\langle\Psi|\mathcal{H}_{\mathrm{e}}|\Psi\rangle$ was not specified in detail. It is immediately clear that *ab initio* molecular dynamics is not tied to any particular approach, although very accurate techniques

are of course prohibitively expensive. It is also evident that the strength or weakness of a particular *ab initio* molecular dynamics scheme is intimately connected to the strength or weakness of the chosen electronic structure method. Over the years a variety of different approaches such as density functional[38, 285, 13, 201, 158, 14], Hartree–Fock[166, 109, 79, 175, 125, 128, 144, 132], generalized valence bond (GVB)[126, 127, 93–95], complete active space SCF (CASSCF)[235, 236], full configuration interaction (FCI)[172], semiempirical[281, 282, 37, 78, 41, 280, 124] or other approximate[202, 191, 232, 192, 67, 68, 8] methods were combined with molecular dynamics, and this list is certainly incomplete.

The focus of the present review clearly is Car–Parrinello molecular dynamics in conjunction with Hohenberg–Kohn–Sham density functional theory[138, 153]. In the following, only those parts of density functional theory are presented that impact directly on *ab initio* molecular dynamics. For a deeper presentation and in particular for a discussion of the assumptions and limitations of this approach (both conceptually and in practice) the reader is referred to the existing excellent literature[247, 147, 194, 66, 176]. For simplicity, the formulae are presented for the spin–unpolarized or restricted special case.

Following the exposition of density functional theory, the fundamentals of Hartree–Fock theory, which is often considered to be the basis of quantum chemistry, are introduced for the same special case. Finally, a glimpse is given at post Hartree–Fock methods. Again, an extensive text–book literature exists for these wave function–based approaches to electronic structure calculations[252, 183]. The very useful connection between the density–based and wave function–based methods goes back to Löwdin's work in the mid fifties and is e.g. worked out in Chapt. 2.5 of Ref. 194, where Hartree–Fock theory is formulated in density–matrix language.

2.7.2 Density Functional Theory

The total ground–state energy of the interacting system of electrons with classical nuclei fixed at positions $\{\mathbf{R}_I\}$ can be obtained

$$\min_{\Psi_0} \{\langle \Psi_0 \, | \mathcal{H}_{\rm e} | \, \Psi_0 \rangle\} = \min_{\{\phi_i\}} E^{\rm KS}[\{\phi_i\}]$$

as the minimum of the Kohn–Sham energy[138, 153]

$$E^{\rm KS}[\{\phi_i\}] = T_{\rm s}[\{\phi_i\}] + \int d\mathbf{r} \;\; V_{\rm ext}(\mathbf{r}) \; n(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} \;\; V_{\rm H}(\mathbf{r}) \; n(\mathbf{r}) + E_{\rm xc}[n] \;\; , \quad (75)$$

which is an explicit functional of the set of auxiliary functions $\{\phi_i(\mathbf{r})\}$ that satisfy the orthonormality relation $\langle \phi_i \mid \phi_j \rangle = \delta_{ij}$. This is a dramatic simplification since the minimization with respect to all possible *many–body* wave functions $\{\Psi\}$ is replaced by a minimization with respect to a set of orthonormal one–particle functions, the Kohn–Sham orbitals $\{\phi_i\}$. The associated electronic one–body density or charge density

$$n(\mathbf{r}) = \sum_i^{\rm occ} f_i \mid \phi_i(\mathbf{r}) \mid^2 \quad (76)$$

is obtained from a single Slater determinant built from the occupied orbitals, where $\{f_i\}$ are integer occupation numbers.

The first term in the Kohn–Sham functional Eq. (75) is the kinetic energy of a non–interacting reference system

$$T_{\rm s}[\{\phi_i\}] = \sum_i^{\rm occ} f_i \left\langle \phi_i \left| -\frac{1}{2}\nabla^2 \right| \phi_i \right\rangle \tag{77}$$

consisting of the same number of electrons exposed to the same external potential as in the fully interacting system. The second term comes from the fixed external potential

$$V_{\rm ext}(\mathbf{r}) = -\sum_I \frac{Z_I}{|\mathbf{R}_I - \mathbf{r}|} + \sum_{I<J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \tag{78}$$

in which the electrons move, which comprises the Coulomb interactions between electrons and nuclei and in the definition used here also the internuclear Coulomb interactions; this term changes in the first place if core electrons are replaced by pseudopotentials, see for instance Ref. 179 for a detailed discussion. The third term is the Hartree energy, i.e. the classical electrostatic energy of two charge clouds which stem from the electronic density and is obtained from the Hartree potential

$$V_{\rm H}(\mathbf{r}) = \int d\mathbf{r}' \ \frac{n(\mathbf{r}')}{|\ \mathbf{r} - \mathbf{r}'\ |} \ , \tag{79}$$

which in turn is related to the density via

$$\nabla^2 V_{\rm H}(\mathbf{r}) = -4\pi n(\mathbf{r}) \tag{80}$$

Poisson's equation. The last contribution in the Kohn–Sham functional, the exchange–correlation functional $E_{\rm xc}[n]$, is the most intricate contribution to the total electronic energy. The electronic exchange and correlation effects are lumped together and basically define this functional as the remainder between the exact energy and its Kohn–Sham decomposition in terms of the three previous contributions.

The minimum of the Kohn–Sham functional is obtained by varying the energy functional Eq. (75) for a fixed number of electrons with respect to the density Eq. (76) or with respect to the orbitals subject to the orthonormality constraint, see e.g. the discussion following Eq. (35) for a similar variational procedure. This leads to the Kohn–Sham equations

$$\left\{ -\frac{1}{2}\nabla^2 + V_{\rm ext}(\mathbf{r}) + V_{\rm H}(\mathbf{r}) + \frac{\delta E_{\rm xc}[n]}{\delta n(\mathbf{r})} \right\} \phi_i(\mathbf{r}) = \sum_j \Lambda_{ij} \phi_j(\mathbf{r}) \tag{81}$$

$$\left\{ -\frac{1}{2}\nabla^2 + V^{\rm KS}(\mathbf{r}) \right\} \phi_i(\mathbf{r}) = \sum_j \Lambda_{ij} \phi_j(\mathbf{r}) \tag{82}$$

$$H_{\rm e}^{\rm KS} \phi_i(\mathbf{r}) = \sum_j \Lambda_{ij} \phi_j(\mathbf{r}) \ , \tag{83}$$

which are one–electron equations involving an effective *one–particle* Hamiltonian $H_{\rm e}^{\rm KS}$ with the local potential $V^{\rm KS}$. Note that $H_{\rm e}^{\rm KS}$ nevertheless embodies the electronic *many–body* effects by virtue of the exchange–correlation potential

$$\frac{\delta E_{\rm xc}[n]}{\delta n(\mathbf{r})} = V_{\rm xc}(\mathbf{r}) \ . \tag{84}$$

A unitary transformation within the space of the occupied orbitals leads to the canonical form

$$H_{\rm e}^{\rm KS}\phi_i = \epsilon_i\phi_i \tag{85}$$

of the Kohn–Sham equations, where $\{\epsilon_i\}$ are the eigenvalues. In conventional static density functional or "band structure" calculations this set of equations has to be solved self–consistently in order to yield the density, the orbitals and the Kohn–Sham potential for the electronic ground state[212]. The corresponding total energy Eq. (75) can be written as

$$E^{\rm KS} = \sum_i \epsilon_i - \frac{1}{2}\int d\mathbf{r}\ V_{\rm H}(\mathbf{r})\ n(\mathbf{r}) + E_{\rm xc}[n] - \int d\mathbf{r}\ \frac{\delta E_{\rm xc}[n]}{\delta n(\mathbf{r})}\ n(\mathbf{r})\ , \tag{86}$$

where the sum over Kohn–Sham eigenvalues is the so–called "band structure energy".

Thus, Eqs. (81)–(83) together with Eqs. (39)–(40) define Born–Oppenheimer molecular dynamics within Kohn–Sham density functional theory, see e.g. Refs. 96, 257, 250, 13, 285, 201, 14, 158, 159 for such implementations. The functional derivative of the Kohn–Sham functional with respect to the orbitals, the Kohn–Sham force acting on the orbitals, can be expressed as

$$\frac{\delta E^{\rm KS}}{\delta\phi_i^\star} = f_i H_{\rm e}^{\rm KS}\phi_i\ , \tag{87}$$

which makes clear the connection to Car–Parrinello molecular dynamics, see Eq. (45). Thus, Eqs. (59)–(60) have to be solved with the effective one–particle Hamiltonian in the Kohn–Sham formulation Eqs. (81)–(83). In the case of Ehrenfest dynamics presented in Section 2.2, which will not be discussed in further detail at this stage, the Runge–Gross time–dependent generalization of density functional theory[110] has to be invoked instead, see e.g. Refs. 83, 258, 223.

Crucial to any application of density functional theory is the approximation of the unknown exchange and correlation functional. A discussion focussed on the utilization of suitable functionals in the framework of *ab initio* molecular dynamics is for instance given in Ref. 245. Those exchange–correlation functionals belong to the class of the "Generalized Gradient Approximation"

$$E_{\rm xc}^{\rm GGA}[n] = \int d\mathbf{r}\ n(\mathbf{r})\ \varepsilon_{\rm xc}^{\rm GGA}(n(\mathbf{r}); \nabla n(\mathbf{r}))\ , \tag{88}$$

where the unknown functional is approximated by an integral over a function that depends only on the density and its gradient at a given point in space, see Ref. 206 and references therein. The combined exchange–correlation function is typically split up into two additive terms $\varepsilon_{\rm x}$ and $\varepsilon_{\rm c}$ for exchange and correlation, respectively. In the simplest case it is the exchange and correlation energy density $\varepsilon_{\rm xc}^{\rm LDA}(n)$ of an interacting but homogeneous electron gas at the density given by the "local" density $n(\mathbf{r})$ at space–point $\mathbf{r}$ in the inhomogeneous system. This simple but astonishingly powerful approximation[147] is the famous local density approximation LDA[153] (or local spin density LSD in the spin–polarized case[16]), and a host of different parameterizations exist in the literature[194, 66, 176]. The self–interaction correction[203] SIC as applied to LDA was critically assessed for molecules in Ref. 98 with a disappointing outcome.

A significant improvement of the accuracy was achieved by introducing the gradient of the density as indicated in Eq. (88) beyond the well–known straightforward gradient

expansions. These so–called GGAs (also denoted as "gradient corrected" or "semilocal" functionals) extended the applicability of density functional calculation to the realm of chemistry, see e.g. Refs. 204, 18, 164, 206, 205, 207 for a few "popular functionals" and Refs. 146, 71, 238, 148, 49, 248, 249 for extensive tests on molecules, hydrogen–bonded complexes, solids, and surfaces.

and Refs. 146, 71, 238, 148 for extensive tests on molecules, complexes, and solids, respectively.

Another considerable advance was the successful introduction of "hybrid functionals"[19,20] that include to some extent "exact exchange"[103] in addition to a standard GGA. Although such functionals can certainly be implemented within a plane wave approach[113,43,179], they are prohibitively time–consuming as explained in Ref. 179. A more promising route in this respect are those functionals that include higher–order powers of the gradient (or the local kinetic energy density) in the sense of a generalized gradient expansion beyond the first term. Promising results could be achieved by including Laplacian or local kinetic energy terms[214,80,81,279,255,31], but at this stage a sound judgment concerning their "prize / performance ratio" has to await further scrutinizing tests. The "optimized potential method" (OPM) or "optimized effective potentials" (OEP) are another route to include "exact exchange" within density functional theory, see e.g. Section 13.6 in Ref. 245 or Ref. 107 for overviews. Here, the exchange–correlation functional $E_{\rm xc}^{\rm OPM} = E_{\rm xc}[\{\phi_i\}]$ depends on the individual orbitals instead of only on the density or its derivatives.

2.7.3 Hartree–Fock Theory

Hartree–Fock theory is derived by invoking the variational principle in a restricted space of wave functions. The antisymmetric ground–state electronic wave function is approximated by a single Slater determinant $\Psi_0 = \det\{\psi_i\}$ which is constructed from a set of one–particle spin orbitals $\{\psi_i\}$ required to be mutually orthonormal $\langle \psi_i | \psi_j \rangle = \delta_{ij}$. The corresponding variational minimum of the total electronic energy $\mathcal{H}_{\rm e}$ defined in Eq. (2)

$$\begin{aligned} E^{\rm HF}[\{\psi_i\}] = & \sum_i \int d\mathbf{r}\, \psi_i^\star(\mathbf{r}) \left[-\frac{1}{2}\nabla^2 + V_{\rm ext}(\mathbf{r}) \right] \psi_i(\mathbf{r}) \\ & + \frac{1}{2} \sum_{ij} \int\int d\mathbf{r}\, d\mathbf{r}'\, \psi_i^\star(\mathbf{r}) \psi_j^\star(\mathbf{r}') \, \frac{1}{|\mathbf{r}-\mathbf{r}'|} \, \psi_i(\mathbf{r}) \psi_j(\mathbf{r}') \\ & + \frac{1}{2} \sum_{ij} \int\int d\mathbf{r}\, d\mathbf{r}'\, \psi_i^\star(\mathbf{r}) \psi_j^\star(\mathbf{r}') \, \frac{1}{|\mathbf{r}-\mathbf{r}'|} \, \psi_j(\mathbf{r}) \psi_i(\mathbf{r}') \end{aligned} \tag{89}$$

yields the lowest energy and the "best" wave function within a one–determinant ansatz; the external Coulomb potential $V_{\rm ext}$ was already defined in Eq. (78). Carrying out the constraint minimization within this ansatz (see Eq. (36) in Section 2.3 for a sketch) leads

to

$$\left\{ -\frac{1}{2}\nabla^2 + V_{\rm ext}(\mathbf{r}) + \sum_j \mathcal{J}_j(\mathbf{r}) - \sum_j \mathcal{K}_j(\mathbf{r}) \right\} \psi_i(\mathbf{r}) = \sum_j \Lambda_{ij} \psi_j(\mathbf{r}) \tag{90}$$

$$\left\{ -\frac{1}{2}\nabla^2 + V^{\rm HF}(\mathbf{r}) \right\} \psi_i(\mathbf{r}) = \sum_j \Lambda_{ij} \psi_j(\mathbf{r}) \tag{91}$$

$$H_{\rm e}^{\rm HF} \psi_i(\mathbf{r}) = \sum_j \Lambda_{ij} \psi_j(\mathbf{r}) \tag{92}$$

the Hartree–Fock integro–differential equations. In analogy to the Kohn–Sham equations Eqs. (81)–(83) these are effective one–particle equations that involve an effective one–particle Hamiltonian $H_{\rm e}^{\rm HF}$, the (Hartree–) Fock operator. The set of canonical orbitals

$$H_{\rm e}^{\rm HF} \psi_i = \epsilon_i \psi_i \tag{93}$$

is obtained similarly to Eq. (85). The Coulomb operator

$$\mathcal{J}_j(\mathbf{r})\ \psi_i(\mathbf{r}) = \left[\int d\mathbf{r}'\ \psi_j^\star(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \psi_j(\mathbf{r}') \right]\ \ \psi_i(\mathbf{r}) \tag{94}$$

and the exchange operator

$$\mathcal{K}_j(\mathbf{r})\ \psi_i(\mathbf{r}) = \left[\int d\mathbf{r}'\ \psi_j^\star(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} \psi_i(\mathbf{r}') \right]\ \ \psi_j(\mathbf{r}) \tag{95}$$

are most easily defined via their action on a particular orbital ψ_i. It is found that upon acting on orbital $\psi_i(\mathbf{r})$ the exchange operator for the j–th state "exchanges" $\psi_j(\mathbf{r}') \rightarrow \psi_i(\mathbf{r}')$ in the kernel as well as replaces $\psi_i(\mathbf{r}) \rightarrow \psi_j(\mathbf{r})$ in its argument, compare to the Coulomb operator. Thus, $\mathcal{K}$ is a non–local operator as its action on a function ψ_i at point $\mathbf{r}$ in space requires the evaluation and thus the knowledge of that function throughout all space by virtue of $\int d\mathbf{r}'\ \psi_i(\mathbf{r}') \ldots$ the required integration. In this sense the exchange operator does not possess a simple classical interpretation like the Coulomb operator $\mathcal{C}$, which is the counterpart of the Hartree potential $V_{\rm H}$ in Kohn–Sham theory. The exchange operator vanishes exactly if the antisymmetrization requirement of the wave function is relaxed, i.e. only the Coulomb contribution survives if a Hartree product is used to represent the wave function.

The force acting on the orbitals is defined

$$\frac{\delta E^{\rm HF}}{\delta \psi_i^\star} = H_{\rm e}^{\rm HF} \psi_i \tag{96}$$

similarly to Eq. (87). At this stage, the various *ab initio* molecular dynamics schemes based on Hartree–Fock theory are defined, see Eqs. (39)–(40) for Born–Oppenheimer molecular dynamics and Eqs. (59)–(60) for Car–Parrinello molecular dynamics. In the case of Ehrenfest molecular dynamics the time–dependent Hartree–Fock formalism[62] has to be invoked instead.

2.7.4 Post Hartree–Fock Theories

Although post Hartree–Fock methods have a very unfavorable scaling of the computational cost as the number of electrons increases, a few case studies were performed with such correlated quantum chemistry techniques. For instance *ab initio* molecular dynamics was combined with GVB[126, 127, 93–95], CASSCF[235, 236], MP2[230], as well as FCI[172] approaches, see also references therein. It is noted in passing that Car–Parrinello molecular dynamics can only be implemented straightforwardly if energy and wave function are "consistent". This is not the case in perturbation theories such as e.g. the widely used Møller–Plesset approach[131]: within standard MP2 the energy is correct to second order, whereas the wave function is the one given by the uncorrelated HF reference. As a result, the derivative of the MP2 energy with respect to the wave function Eq. (96) does not yield the correct force on the HF wave function in the sense of fictitious dynamics. Such problems are of course absent from the Born–Oppenheimer approach to sample configuration space, see e.g. Ref. 150, 145, 11 for MP2, density functional, and multireference CI *ab initio* Monte Carlo schemes or Ref. 230 for a recent Born–Oppenheimer molecular dynamics simulation using MP2 energies and forces.

It should be kept in mind that the rapidly growing workload of post HF calculations, although extremely powerful in principle, limits the number of explicitly treated electrons to only a few. The rapid development of correlated electronic structure methods that scale linearly with the number of electrons will certainly broaden the range of applicability of this class of techniques in the near future.

2.8 Basis Sets

2.8.1 Gaussians and Slater Functions

Having selected a specific electronic structure method the next choice is related to which basis set to use in order to represent the orbitals ψ_i in terms of simple analytic functions f_ν with well–known properties. In general a *linear* combination of such basis functions

$$\psi_i(\mathbf{r}) = \sum_\nu c_{i\nu} f_\nu(\mathbf{r}; \{\mathbf{R}_I\}) \tag{97}$$

is used, which represents exactly any reasonable function in the limit of using a complete set of basis functions. In quantum chemistry, Slater–type basis functions (STOs)

$$f^{\mathrm{S}}_{\mathbf{m}}(\mathbf{r}) = N^{\mathrm{S}}_{\mathbf{m}}\, r_x^{m_x} r_y^{m_y} r_z^{m_z}\, \exp\left[-\zeta_{\mathbf{m}}|\mathbf{r}|\right] \tag{98}$$

with an exponentially decaying radial part and Gaussian–type basis functions (GTOs)

$$f^{\mathrm{G}}_{\mathbf{m}}(\mathbf{r}) = N^{\mathrm{G}}_{\mathbf{m}}\, r_x^{m_x} r_y^{m_y} r_z^{m_z}\, \exp\left[-\alpha_{\mathbf{m}} r^2\right] \tag{99}$$

have received widespread use, see e.g. Ref. 131 for a concise overview–type presentation. Here, $N_{\mathbf{m}}$, $\zeta_{\mathbf{m}}$ and $\alpha_{\mathbf{m}}$ are constants that are typically kept fixed during a molecular electronic structure calculation so that only the orbital expansion coefficients $c_{i\nu}$ need to be optimized. In addition, fixed linear combinations of the above–given "primitive" basis functions can be used for a given angular momentum channel $\mathbf{m}$, which defines the "contracted" basis sets.

The Slater or Gaussian basis functions are in general centered at the positions of the nuclei, i.e. $\mathbf{r} \to \mathbf{r} - \mathbf{R}_I$ in Eq. (98)–(99), which leads to the linear combination of *atomic*

orbitals (LCAO) ansatz to solve differential equations algebraically. Furthermore, their derivatives as well as the resulting matrix elements are efficiently obtained by differentiation and integration in real–space. However, Pulay forces (see Section 2.5) will result for such basis functions that are fixed at atoms (or bonds) if the atoms are allowed to move, either in geometry optimization or molecular dynamics schemes. This disadvantage can be circumvented by using *freely* floating Gaussians that are distributed in space[241], which form an originless basis set since it is localized but not atom–fixed.

A first generation of methods using Gaussian basis functions in the context of *ab initio* molecular dynamics has been proposed roughly in the early to mid nineties in the sense of interfacing existing electronic structure codes with a driver for molecular dynamics, see for instance Refs. 109, 79, 175, 125–128, 93, 144, 132, 172, 94, 95, 235, 236. More recently, a second generation of such approaches that do more explicitly take advantage of the dynamical evolution of the electronic degrees of freedom, which is conceptually at the very root of the efficiency of the original Car–Parrinello algorithm, is developed in the framework of Car–Parrinello[229, 230, 221, 136], Born–Oppenheimer[137, 277] and Ehrenfest[169] dynamics schemes.

2.8.2 Plane Waves

A vastly different approach has its roots in solid–state theory. Here, the ubiquitous periodicity of the underlying lattice produces a periodic potential and thus imposes the same periodicity on the density (implying Bloch's Theorem, Born–von Karman periodic boundary conditions etc., see e.g. Chapt. 8 in Ref. 9). This heavily suggests to use plane waves as the generic basis set in order to expand the periodic part of the orbitals. Plane waves are defined as

$$f_{\mathbf{G}}^{\mathrm{PW}}(\mathbf{r}) = N \exp\left[i\,\mathbf{G}\mathbf{r}\right] \quad , \tag{100}$$

where the normalization is simply given by $N = 1/\sqrt{\Omega}$; Ω is the volume of the periodic (super–) cell. Since plane waves form a complete and orthonormal set of functions they can be used to expand orbitals according to Eq. (97), where the labeling ν is simply given by the vector $\mathbf{G}$ in reciprocal space / G–space (including only those $\mathbf{G}$–vectors that satisfy the particular periodic boundary conditions). The total electronic energy is found to have a particularly simple form when expressed in plane waves[143].

It is important to observe that plane waves are originless functions, i.e. they do *not* depend on the positions of the nuclei $\{\mathbf{R}_I\}$. This implies that the Pulay forces Eq. (67) vanish exactly even within a *finite* basis (and using a fixed number of plane waves, see the discussion related to "Pulay stress" in Section 2.5), which tremendously facilitates force calculations. This also implies that plane waves are a very unbiased basis set in that they are "delocalized" in space and do not "favor" certain atoms or regions over others, i.e. they can be considered as an ultimately "balanced basis set" in the language of quantum chemistry. Thus, the only way to improve the quality of the basis is to increase the "energy cutoff" E_{cut}, i.e. to increase the largest $|\mathbf{G}|$–vector that is included in the finite expansion Eq. (97). This blind approach is vastly different from the traditional procedures in quantum chemistry that are needed in order to produce reliable basis sets[131]. Another appealing feature is that derivatives in real–space are simply multiplications in G–space, and both spaces can be efficiently connected via Fast Fourier Transforms (FFTs). Thus, one can

easily evaluate operators in that space in which they are diagonal, see for instance the flow charts in Ref. 179.

According to the well–known "No Free Lunch Theorem" there cannot be only advantages connected to using plane waves. The first point is that the pseudopotential approximation is intimately connected to using plane waves, why so? A plane wave basis is basically a lattice–symmetry–adapted three–dimensional Fourier decomposition of the orbitals. This means that increasingly large Fourier components are needed in order to resolve structures in real space on decreasingly small distance scales. But already orbitals of first row atoms feature quite strong and rapid oscillations close to the nuclei due to the Pauli principle, which enforces a nodal structure onto the wave function by imposing orthogonality of the orbitals. However, most of chemistry is ruled by the valence electrons, whereas the core electrons are essentially inert. In practice, this means that the innermost electrons can be taken out of explicit calculations. Instead they are represented by a smooth and nodeless effective potential, the so–called pseudopotential[134, 135, 209, 210, 50], see for instance Refs. 212, 239, 90 for reviews in the context of "solid state theory" and Refs. 53, 64 for pseudopotentials as used in "quantum chemistry". The resulting pseudo wave function is made as smooth as possible close to the nuclear core region. This also means that properties that depend crucially on the wave function close to the core cannot be obtained straightforwardly from such calculations. In the field of plane wave calculations the introduction of "soft" norm–conserving *ab initio* pseudopotentials was a breakthrough both conceptually[119] and in practice[10]. Another important contribution, especially for transition metals, was the introduction of the so–called ultrasoft pseudopotentials by Vanderbilt[276]. This approaches lead to the powerful technique of plane wave pseudopotential electronic structure calculations in the framework of density functional theory[143, 212]. Within this particular framework the issue of pseudopotentials is elaborated in more detail in Ref. 179.

Another severe shortcoming of plane waves is the backside of the medal of being an unbiased basis set: there is no way to shuffle more basis functions into regions in space where they are more needed than in other regions. This is particularly bad for systems with strong inhomogeneities. Such examples are all–electron calculations or the inclusion of semi–core states, a few heavy atoms in a sea of light atoms, and (semi–) finite systems such as surfaces or molecules with a large vacuum region in order to allow the long–range Coulomb interactions to decay. This is often referred to as the multiple length scale deficiency of plane wave calculations.

2.8.3 Generalized Plane Waves

An extremely appealing and elegant generalization of the plane wave concept[114, 115] consists in defining them in curved ξ–space

$$f_{\mathbf{G}}^{\mathrm{GPW}}(\xi) = N \det{}^{1/2} J \exp\left[i\mathbf{G}\,\mathbf{r}(\xi)\right] \qquad (101)$$
$$\det J = \left|\frac{\partial r^i}{\partial \xi^j}\right| \quad ,$$

where $\det J$ is the Jacobian of the transformation from Cartesian to curvilinear coordinates $\mathbf{r} \rightarrow \xi(\mathbf{r})$ with $\xi = (\xi^1, \xi^2, \xi^3)$ and $N = 1/\sqrt{\Omega}$ as for regular plane waves. These functions are orthonormal, form a complete basis set, can be used for $\mathbf{k}$–point sampling after replacing $\mathbf{G}$ by $\mathbf{G} + \mathbf{k}$ in Eq. (101), are originless (but nevertheless localized) so that

Pulay forces are absent, can be manipulated via efficient FFT techniques, and reduce to standard plane waves in the special case of an Euclidean space $\xi(\mathbf{r}) = \mathbf{r}$. Thus, they can be used equally well like plane waves in linear expansions of the sort Eq. (65) underlying most of electronic structure calculations. The Jacobian of the transformation is related to the Riemannian metric tensor

$$g_{ij} = \sum_{k=1}^{3} \frac{\partial \xi^k}{\partial r^i} \frac{\partial \xi^k}{\partial r^j}$$
$$\det J = \det{}^{-1/2} \{g_{ij}\} \tag{102}$$

which defines the metric of the ξ–space. The metric and thus the curvilinear coordinate system itself is considered as a variational parameter in the original fully adaptive–coordinate approach[114,115], see also Refs. 60, 120–123. Thus, a uniform grid in curved Riemannian space is non–uniform or distorted when viewed in flat Euclidean space (where $g_{ij} = \delta_{ij}$) such that the density of grid points (or the "local" cutoff energy of the expansion in terms of G–vectors) is highest in regions close to the nuclei and lowest in vacuum regions, see Figure 2 in Ref. 120.

Concerning actual calculations, this means that a lower number of generalized plane waves than standard plane waves are needed in order to achieve a given accuracy[114], see Figure 1 in Ref. 120. This allows even for all–electron approaches to electronic structure calculations where plane waves fail[186,217]. More recently, the distortion of the metric was frozen spherically around atoms by introducing deformation functions[116,117], which leads to a concept closely connected to non–uniform atom–centered meshes in real–space methods[186], see below. In such non–fully–adaptive approaches using *predefined* coordinate transformations attention has to be given to Pulay force contributions which have to be evaluated explicitly[116,186].

2.8.4 Wavelets

Similar to using generalized plane waves is the idea to exploit the powerful multiscale–properties of wavelets. Since this approach requires an extensive introductory discussion (see e.g. Ref. 100 for a gentle introduction) and since it seems still quite far from being used in large–scale electronic structure calculations the interested reader is referred to original papers[46,283,290,273,99] and review articles[7,102]. Wavelet–based methods allow intrinsically to exploit multiple length scales without introducing Pulay forces and can be efficiently handled by fast wavelet transforms. In addition, they are also a powerful route to linear scaling or "order–N" methods[190,101] as first demonstrated in Ref. 99 with the calculation of the Hartree potential for an all–electron uranium dimer.

2.8.5 Mixed and Augmented Basis Sets

Localized Gaussian basis functions on the one hand and plane waves on the other hand are certainly two extreme cases. There has been a tremendous effort to combine such localized and originless basis functions in order to exploit their mutual strengths. This resulted in a rich collection of mixed and augmented basis sets with very specific implementation requirements. This topic will not be covered here and the interested reader is referred to Refs. 28, 274, 219, 170, 171, 277 and references given therein for some recent implementations used in conjunction with *ab initio* molecular dynamics.

2.8.6 Wannier Functions

An alternative to the plane wave basis set in the framework of periodic calculations in solid–state theory are Wannier functions, see for instance Section 10 in Ref. 9. These functions are formally obtained from a unitary transformation of the Bloch orbitals and have the advantage that they can be exponentially localized under certain circumstances. The so–called maximally localized generalized Wannier functions[182] are the periodic analogues of Boys' localized orbitals defined for isolated systems. Recently the usefulness of Wannier functions for numerical purposes was advocated by several groups, see Refs. 154, 75, 182, 2, 165 and references given therein.

2.8.7 Real Space Grids

A quite different approach is to leave conventional basis set approaches altogether and to resort to real–space methods[17] where continuous space is replaced by a discrete space $\mathbf{r} \rightarrow r_{\mathbf{p}}$. This entails that the derivative operator or the entire energy expression has to be discretized in some way. The high–order central–finite difference approach leads to the expression

$$
\begin{aligned}
-\frac{1}{2}\nabla^2\psi_i(\mathbf{r}) \stackrel{h\rightarrow 0}{=} -\frac{1}{2}\Bigg[& \sum_{n_x=-N}^{N} C_{n_x}\ \psi_i(r_{p_x}+n_x h, r_{p_y}, r_{p_z}) \\
& + \sum_{n_y=-N}^{N} C_{n_y}\ \psi_i(r_{p_x}, r_{p_y}+n_y h, r_{p_z}) \\
& + \sum_{n_z=-N}^{N} C_{n_z}\ \psi_i(r_{p_x}, r_{p_y}, r_{p_z}+n_z h)\Bigg] + \mathcal{O}\left(h^{2N+2}\right) \quad (103)
\end{aligned}
$$

for the Laplacian which is correct up to the order h^{2N+2}. Here, h is the uniform grid spacing and $\{C_{\mathbf{n}}\}$ are known expansion coefficients that depend on the selected order[44]. Within this scheme, not only the grid spacing h but also the order are disposable parameters that can be optimized for a particular calculation. Note that the discretization points in continuous space can also be considered to constitute a sort of "finite basis set" – despite different statements in the literature – and that the "infinite basis set limit" is reached as $h \rightarrow 0$ for N fixed. A variation on the theme are Mehrstellen schemes where the discretization of the entire differential equation and not only of the derivative operator is optimized[36].

The first real–space approach devised for *ab initio* molecular dynamics was based on the lowest–order finite–difference approximation in conjunction with a equally–spaced cubic mesh in real space[39]. A variety of other implementations of more sophisticated real–space methods followed and include e.g. non–uniform meshes, multigrid acceleration, different discretization techniques, and finite–element methods[286, 23, 15, 44, 45, 259, 260, 186, 261, 3, 231], see Ref. 17 for a review. Among the chief advantages of the real–space methods is that linear scaling approaches[190, 101] can be implemented in a natural way and that the multiple–length scale problem can be coped with by adapting the grid. However, the extension to such non–uniform meshes induces the (in)famous Pulay forces (see Section 2.5) if the mesh moves as the nuclei move.

3 Summary and Outlook

The essentials of what is now called standard ab initio molecular dynamics have been reviewed in this Keynote Lecture whereas more advanced approaches are covered in other Lectures at the *NIC Winter School 2006* "Computational Nanoscience: Do it Yourself!". The notion "standard" implies here the adiabatic propagation in the Born–Oppenheimer ground–state, the usage of classical nuclei and the generation of trajectories in the micro-canonical ensemble. This is a mature computer simulation technique by now and a growing number of powerful computer codes able to perform *ab initio* molecular dynamics simulations in this spirit is available such as for instance the ABINIT[1], CASTEP[42], CPMD[139] CP-PAW[52], CP2k[51], Dacapo[54], fhi98md[77], NWChem[189], PINY[213], PWscf/Quantum-ESPRESSO[218], S/PHI/nX[240], or VASP[278] packages among others. It is not difficult to predict that the expanding family of ab initio molecular dynamics techniques, which might differ in the underlying electronic structure theory, the propagation scheme, the basis set or other technical aspects, will have an ever increasing impact on the simulation of "chemically complex" molecular systems.

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